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Licenciada em Ciências da Engenharia Química e Bioquímica

Case Study for N_2O Purification in a Wastewater Treatment Plant, through an Economic Analysis

Dissertação para obtenção do Grau de Mestre em

Engenharia Química e Bioquímica

Orientador: Eng. Pedro Póvoa, Águas de Portugal

Co-orientador: Dr. Adrian Oehmen, FCT-UNL

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FACULDADE DE CIÊNCIAS E TECNOLOGIA
UNIVERSIDADE NOVA DE LISBOA

Março 2016

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But if you judge a fish on its ability to climb a tree,
it will live its whole life believing that it is stupid.

Albert Einstein

Acknowledgements

This project, consuming a huge amount of work and research, as well as effort and dedication not only from myself but from all my tutors, would not have been possible without the support and help from all the people involved.

To Lord God Almighty, for the completion of this work. Only due to his blessings I could finish my master thesis.

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To my beloved parents, and family, as always, helped me economically. A very special thanks for making this amazing journey possible and also for their tireless support in every moment of my life.

To my sister for her patience.

Resumo

O presente estudo é focado numa avaliação para a recuperação do óxido nitroso (N_2O) em Estações de Tratamento de Águas Residuais (ETARs). Nos últimos anos, os custos operacionais das ETARs aumentaram principalmente devido aos aumentos no custo de energia. Os métodos estabelecidos para a purificação das águas residuais têm a desvantagem do grande consumo de energia, pelo que é necessário explorar potenciais para economizar os sistemas estabelecidos.

Uma ETAR em larga escala tem o potencial para a produção de N_2O e combinando a possibilidade de tratamento de águas residuais com a produção de combustível (CH_4), associada à redução de gases efeito estufa (recuperação N_2O), abre uma nova dimensão no ciclo da água e realmente representa os termos-chave para uma economia sustentável e circular. Três cenários avaliam a possibilidade para a purificação do gás N_2O, numa ETAR em particular localizada em Alcântara (Portugal). A seguinte avaliação é apresentada:

Caso	Cenário 1	Cenário 2	Cenário 3
Purificação N_2O	24%	24%	99.7%
Pressão	Sistema a vácuo	Até 3 bar	Até 44 bar
Propósito	Pré-tratamento biogás	Pré-tratamento biogás	Receita adicional
Purificação Final N_2O	68%	68%	99.7%
Objetivo	**Combustão do biogás**	**Combustão do biogás**	**Vender N_2O**

O uso de membranas e bombas a vácuo têm lugar no primeiro cenário, que compromete um sistema a vácuo. O segundo cenário, tem um sistema de compressão até 3 bar, seguido por um sistema de arrefecimento e também por membranas. O terceiro cenário tem um sistema de compressão até 44 bar, que também é seguido por sistemas de arrefecimento e membranas, e ainda comprometendo colunas de adsorção com regeneração e uma unidade de liquefação. As folhas de balanços (secção Flowsheet) e os diagramas de instrumentação e tubagens (secção P&ID), relativo a cada cenário, também são apresentados nesta tese.

Uma análise económica para cada cenário também está incluída no presente estudo, para uma possível oportunidade de investimento. Particularmente, o primeiro cenário seria o projeto mais propício a seguir em frente, com um significante baixo grau de risco. A ETAR de Alcântara tem um valor de retorno de 0,10 € por kWh de energia gerada pela combustão do biogás. No terceiro cenário, estima-se 4 € por kg de N_2O vendido. Os seguintes resultados são apresentados:

Caso	Cenário 1	Cenário 2	Cenário 3
Investimento Total (CAPEX)	95,925 €	298,429 €	1,855,189 €
Período de retorno de capital	4 meses	superior a 10 anos	2 anos e 9 meses
Valor Atual Líquido (VAL)	1,718,792 €	- 673,462 €	3,549,223 €
Taxa Interna de Retorno (TIR)	269 %	Inferior a 7 %	40 %
Taxa mínima de atratividade	14 %	14 %	14 %
Ponto Crítico (BEP)	11.7 %	-	47.0 %

Palavras-chave: N_2O, Gás Efeito Estufa, ETAR, Três Cenários, Oportunidade de Investimento, Economia Sustentável.

Abstract

The present study is focused on the evaluation of nitrous oxide (N_2O) recovery in Wastewater Treatment Plants (WWTPs). In the recent years, the operating costs of WWTPs have increased substantially due to the increases in the unit cost of energy. The established methods for wastewater purification have a substantial disadvantage which is the higher energy consumption, and saving potentials need to be explored.

A full-scale WWTP brings the potential of N_2O production. Combining the possibility of wastewater treatment with fuel production (CH_4) associated to greenhouse gases reduction (N_2O recovery) opens a new dimension in water cycle, and really represents the key terms of sustainably and circular economy. Three case scenarios evaluate the possibility for N_2O gas purification in a particular WWTP, located in Alcântara (Portugal). The following evaluation is presented:

Case	Scenario 1	Scenario 2	Scenario 3
N_2O Purification	24%	24%	99.7%
Pressure	Vacuum system	Up to 3 bar	Up to 44 bar
Purpose	Biogas Pre-treatment	Biogas pre-treatment	Additional Revenue
Final N_2O Purification	68%	68%	99.7%
Objective	**Biogas Combustion**	**Biogas Combustion**	**Selling N_2O**

The use of membranes and suction pumps take place in the first case scenario, which has a vacuum system. The second case scenario has a compression system up to 3 bar, which is followed by a cooling system and also membranes. The third case scenario has a compression system up to 44 bar, also followed by cooling systems and membranes, and still having continuous swing adsorption and a unit of liquefaction. Flow balances (Flowsheet section) and piping and instrumentation diagrams (P&ID section), of each case scenario, are also presented in this thesis.

An economic analysis of each case scenario is also included in the present study, for a possible investment opportunity. Particularly, the first case scenario would be the project most likely to go ahead, with a significantly low degree of risk. Alcântara's WWTP has a return value of 0.10 € per kWh of generated energy through biogas combustion. In the third case scenario, it is estimated 4 € per kg for the selling product (N_2O). The following results are presented:

Case	Scenario 1	Scenario 2	Scenario 3
Total Investment (CAPEX)	95,925 €	298,429 €	1,855,189 €
Payback Period	4 months	more than 10 years	2 years + 9 months
Net Present Value (NPV)	1,718,792 €	- 673,462 €	3,549,223 €
Internal Rate of Return (IRR)	269 %	less than 7 %	40 %
Hurdle Rate	14 %	14 %	14 %
Break-even Point (BEP)	11.7 %	-	47.0 %

Keywords: N_2O, Greenhouse Gas, WWTP, Three Case Scenarios, Investment Opportunity, Sustainably Economy.

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List of Abbreviations

AC – Activated Carbon
AOA – Ammonium-oxidizing archaea
AOB – Ammonium-oxidizing bacteria
Anammox – Anaerobic ammonium oxidation bacteria
BEP – Break-even Point
BOD – Biochemical Oxygen Demand (Biodegradable COD)
BOD_L – Liquid BOD
CAPEX – Capital Expenditure
CAS – Chemical Abstracts Service
CEPCI – Chemical Engineering Plant Cost Index
CANDO – Coupled Aerobic-anoxic Nitrous Decomposition Operation
CANON – Completely Autotrophic Nitrogen Removal Over Nitrite
COD – Chemical Oxygen Demand
DEN – Denitrifying bacteria
DGAOs – Denitrifying glycogen-accumulating organisms
DO – dissolved oxygen
DPAOs – Denitrifying polyphosphate-accumulating organisms
EPA – Environmental Protection Agency
EU-28 – European Union comprising 28 member states
e.g. – for example
FCT/UNL – Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa
GAC – Granular Activated Carbon
GHGs – Greenhouse gases
GHG – Greenhouse gas
GWP – Global Warming Potential
IHS – Information Handling Services
IRR – Internal Rate of Return
IUPAC – International Union of Pure and Applied Chemistry
i.e. – that is, namely, in other words
Lab – Laboratory
LUCF – Land-Use Change and Forestry
Nitrox – Gas Mixture Composed of Nitrogen
NOB – Nitrite-oxidizing bacteria
NOD – Nitrogenous Oxygen Demand
NPV – Net Present Value
OLAND – Oxygen-limited Autotrophic Nitrification-denitrification
OPEX – Operational Expenditure
PE – Population Equivalents

P&ID – Piping and Instrumentation Diagram

SBR – sequencing batch reactor

SBRs – sequencing batch reactors

SHARON – Single reactor system for High activity Ammonium Removal Over Nitrite

SNDPR – Simultaneous Nitrogen and Phosphorus Removal

SRT – Solids residence time

ThOD – Theoretical Oxygen Demand

TKN – Total Kjeldahl Nitrogen

TN – Total Nitrogen

U.K. – United Kingdom

UNFCCC – United Nations Framework Convention on Climate Change

U.S.A. – United States of America

U.S. – United States

WWTP – Wastewater Treatment Plant

WWTPs – Wastewater Treatment Plants

List of Units and Symbols

CF_4 – Tetrafluoromethane

CH_4 – Methane

CO_2 – Carbon dioxide

e^- – Electron

HNO_3 – Nitric acid

H_2O – Water

$H_2O_{(L)}$ – Liquid water

H^+ – Hydrogen ion

H_2S – Hydrogen sulphide

N – Nitrogen

N_2 – Dinitrogen

N_2O – Nitrous Oxide

N_2H_4 – Hydrazine

NH_3 – Ammonia

NH_4^+ – Ammonium ion

NH_2OH – Hydroxylamine

NH_4NO_3 – Ammonium nitrate

NO – Nitric oxide

NO_2 – Nitrogen dioxide

NO_2^- – Nitrite ion

NO_3^- – Nitrate ion

NO_x – Nitrogen oxides

O_2 – Dioxygen

PO_4 – Phosphate

PO_4^{3-} – Phosphate ion

P – Phosphorous

SF_6 – Sulfur hexafluoride

acfm – actual cubic foot per minute

bar – Pressure unit (1 bar = 14.504 psi = 0.1 MPa)

cfm – cubic foot per minute (1 cfm = 0.0283 m^3 min^{-1})

cP – centipoises

ft^2 – square foot (1 ft^2 = 0.093 m^2)

g – gram (weight)

gall – gallon (1 U.S. gallon = 3.79 dm^3 = 0.0038 m^3)

h – hour

hp – horsepower (1 horsepower = 745.7 W = 0.746 kW)

in – inch'' (1 '' = 0.0254 m)

kJ – kilojoule

km – kilometer

kt – kilotons

L – liter

m – meter

m^2 – square meter

m^3 – cubic meter

mm – millimeter

mol – mole

mmHg – Millimeter of mercury

min – Minute

mg – milligram

MT CO_2 Eq. – Metric tons CO_2 equivalent

Pa – Pascal

pH – potential hydrogen

ppm – Parts per million

ppmv – Parts per million by volume

ppt – Parts per trillion

psi – Pound per square inch (1 psi = 0.0689 bar)

s – second

tons - tonnes

W – watt

µ – Micro

> – higher than

. – symbol for the decimal separator

, – symbol for the thousand separator

% – Percent

ºC – Celsius degree

& – and

$\Delta\widehat{H}_R^0$ – Standard enthalpy of reaction

ºF – Fahrenheit degree

± – More and less

1. Introduction and Objectives

Fossil fuels are the most utilized source of fuel energy. They are abundant and highly energy dense, making them a desirable source of energy (Alternative Energy, 2013). However, they are also responsible for many of our greatest environmental problems. These problems include global warming, air quality deterioration, oil spills, and acid rain. Nitrogen oxides, products of fossil fuel combustion, contribute to the formation of smog that can irritate the lungs, especially those of people that have asthma, cause bronchitis and pneumonia, and decrease resistance to respiratory infections.

Renewable and alternative energy sources provide a method of energy generation that does not rely on fossil fuels. Photovoltaic solar panels, wind turbines, and hydroelectric generators are examples of renewable technologies that produce electricity and are currently being developed and marketed, resulting in an increase of their use (Department of Energy Resources, 2012). Another way in which fossil fuels can be replaced is by using renewable or alternative sources to produce heat energy that would have otherwise been derived from fuel oil or natural gas.

Parallel to this, domestic wastewater utilities face a challenge of optimizing processes in order to reduce energy consumption and reduce the emission of greenhouse gases (GHGs) arising from wastewater drainage and treatment without compromising discharge permits to which they are subjected. In spite of the progress made in the last decades, a large percentage of water and wastewater systems in Europe and in the rest of the world are still being operated below optimum achievable performances, where considerable savings are possible by optimizing its design and operation. It´s important to notice that drinking water and wastewater systems account for approximately 3–4 percent of energy use in the United States, resulting in the emissions of more than 45 million tons of GHGs annually (U.S. EPA, 2012b).

Nitrous oxide (N_2O) is an extremely potent GHG and it is often incidentally generated in domestic wastewater treatment plants (WWTPs) at levels that are low but still problematic for GHG emissions. As such, researchers have never attempted to maximize N_2O production rates but have instead focused on minimizing/eliminating N_2O production in WWTPs [1].

In addition to N_2O, loss of other forms of reactive nitrogen to natural systems has led to public health problems, including ammonia toxicity to aquatic life, eutrophication of nutrient limited natural water bodies, oxygen depletion and vast dead zones in the ocean margins. It is thus apparent that approaches to N_2O mitigation must be accompanied by strategies to control reactive nitrogen to natural environments [1].

Recently, a new process for the removal of nitrogen from wastewater is introduced. This new process could permit the production on N_2O. Nitrous oxide can act as a powerful oxidant in combustion reactions. It is commonly used to supercharge the engines of high performance vehicles (i.e. *Nitrox*) and as an oxidant in hybrid rocket motors in the aerospace industry [2].

For this reason this thesis is focused on the possibility for N_2O recovery in a WWTP, through an economic analysis. Three case scenarios of N_2O gas purification are evaluated in order to find out whether they'll be viable and economically safe to be applied in Alcântara's WWTP (Portugal).

2. Literature Review

2.1 Greenhouse Gases (GHGs)

The two most abundant gases in the atmosphere nitrogen (N_2), comprising 78% of the dry atmosphere, and oxygen (O_2), comprising 21%, exert almost no greenhouse effect. Instead, the greenhouse effect comes from molecules that are more complex and much less common. Those trap heat in the atmosphere and so are named greenhouse gases (GHGs) [3].

This section provides information based on emissions of the main GHGs. The values are not usually measured directly but instead are estimated through the application of formulas that link emissions to data on generally reported parameters (Foley and Land, 2009).

2.2 GHGs Emissions

Greenhouse gas emissions are typically expressed in metric tons (MT) carbon dioxide (CO_2) equivalent, since this universal standard measurement allows for the comparison of different GHGs based on their ability to trap heat in the atmosphere [4].

Since 1990 the amount of GHGs emitted into the atmosphere was equivalent to more than 30 million metric tons of CO_2, according to World Resources Institute. In fact, the concentration of total GHGs in the atmosphere has increased over the years. However, emissions can rise and fall due to changes in economy, such as, the price of fuel [6]. One of the greatest global financial crises of crude oil prices was in 2009, which led to a small decrease of the emissions by the year [7]. Global emissions of GHGs are presented in Figure 1.

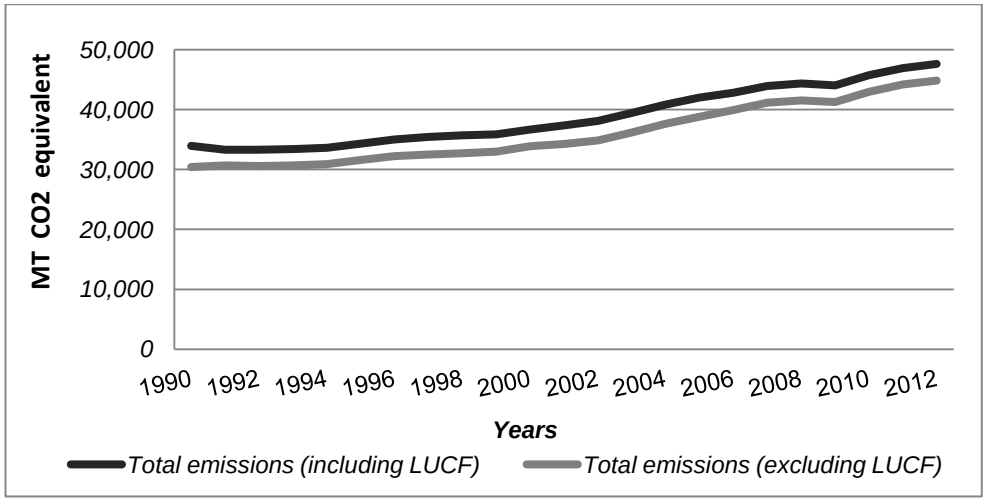

Figure 1 – Global GHGs Emissions (Appendix I, Table 82).
World Resources Institute[1] [5]

[1] The most recent year for public inventory submissions of global GHGs by World Resources Institute is 2012.

Land-Use Change and Forestry (LUCF) is defined by the United Nations Climate Change as a GHG inventory sector resulting from direct human-induced land-use change and forestry activities [8].

The world's top emitters are Asia, United States of America and Europe. Over the years, these countries represented an emission equivalent to more than half of the global GHGs emissions. The emissions growth of China is driven by China's rapid economic and industrial growth and its reliance on fossil fuels [9]. Portugal only represents a small part of the global GHGs emissions equivalent to more than 60 metric tons of CO_2 over the years. Emissions of GHGs by top emitters, and other selected countries, are presented in Figure 2.

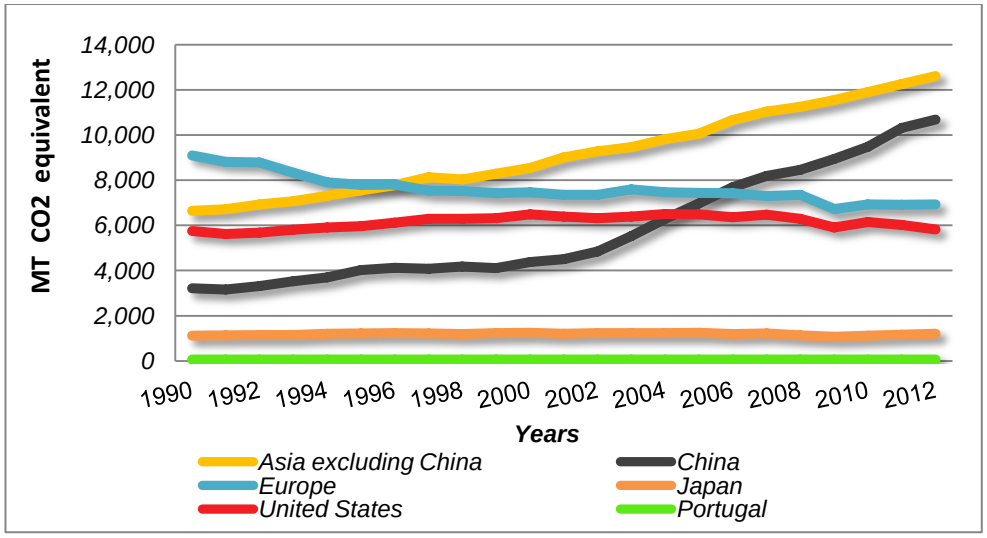

Figure 2 – Total GHGs Emissions, including LUCF, of Top Emitters and from Selected Countries (Appendix I, Table 83). World Resources Institute [5]

The negative effects of climate change will be felt all over the world, and actually the consequences are expected to be most severe in least-developed nations which have produced few emissions [10].

There are many types of greenhouse gases, and some gases are more effective at warming the atmosphere than others because they trap heat more effectively and longer. Each of these gases can remain in the atmosphere for different amounts of time [4]. N_2O is a potent greenhouse gas (298 times more powerful than CO_2).

Global atmospheric concentration, atmospheric lifetime and global warming potential (GWP) of selected GHGs are presented in Table 1.

Table 1 – Global Atmospheric Concentration, Atmospheric Lifetime and Global Warming Potencial (for 100-year time horizon) of Selected GHGs [11].

GHG	Concentration	Lifetime (years)	GWP
CO_2	399 ppm	-	1
CH_4	1.762-1.893 ppm	12	25
N_2O	0.324-0.326 ppm	114	298
SF_6	7.39-7.79 ppt	3,200	22,800
CF_4	79 ppt	> 50,000	7,390

The relationship between kilotons of a gas and metric tons (MT) CO_2 equivalent can be expressed as Equation 1.

$$MT\ CO_2\ Eq. = (kt\ of\ a\ gas) \times (GWP) \times \left(\frac{MT}{1{,}000\ kt}\right) \times 1000$$

Equation 1 – Calculation of MT CO_2 Equivalent [11].

The Kyoto Protocol sets limits on total emissions by the world's major economies [10]. Global GHGs emissions by gas are presented in Figure 3. As expected, powerful GHGs have the lowest gas emissions as compared to CO_2 emission. On the other hand, they have higher GWP meaning a much greater greenhouse effect.

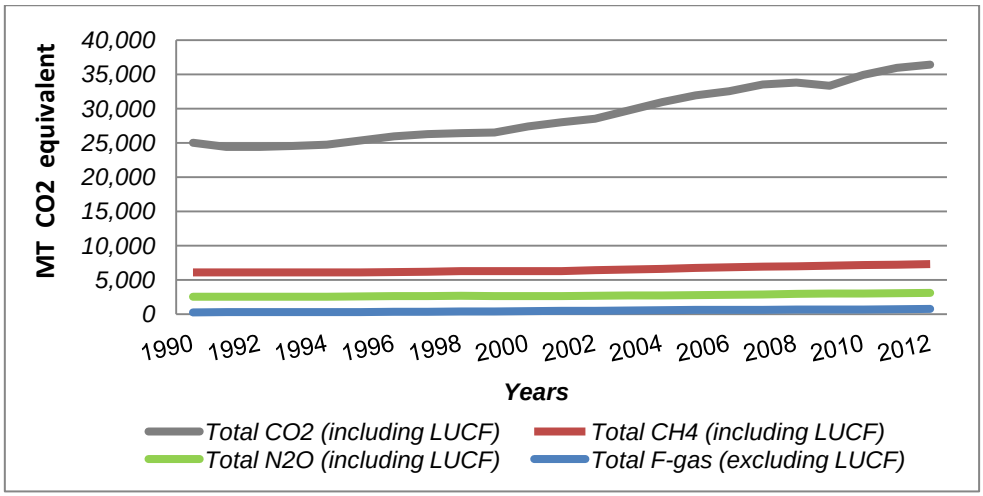

Figure 3 – Global GHGs Emissions by Gas[2] (Appendix I, Table 84). World Resources Institute [5]

Human activities, primarily the burning of fossil fuels for electricity, heat and transportation (which represents part of the energy sector) have greatly intensified the natural greenhouse effect. Global GHGs emissions by sector are presented in Figure 4.

[2] Land-Use Change and Forestry (LUCF) doesn't include F-gas emission.

Waste sector, which mainly includes solid waste disposal on land, biological treatment of solid waste, incineration and open burning of waste, and also wastewater handling [11], hasn't exceed more than 2 million metric tons CO_2 equivalent over the years.

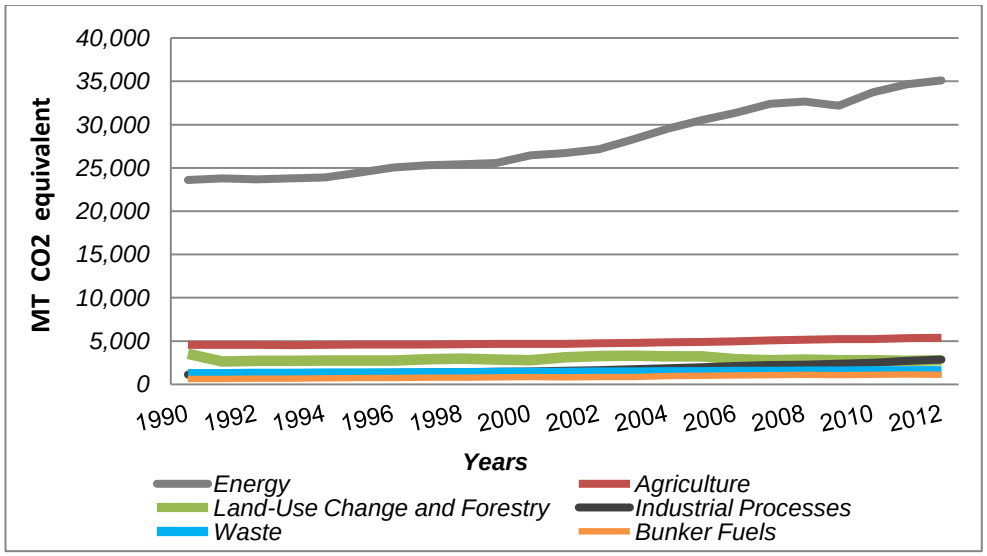

Figure 4 – Global GHGs Emissions by Sector (Appendix I, Table 86). World Resources Institute [5]

2.3 GHGs Emissions from Domestic WWTPs

Wastewater handling includes industrial and domestic wastewater treatment processes. Emissions from domestic WWTPs are mainly methane (CH_4) and nitrous oxide (N_2O) [11]. Figures 5 and 6 present CH_4 and N_2O emissions, respectively, from domestic WWTPs of selected countries. In 2013, emission from Portugal's domestic WWTPs was equivalent to 35.2 kt of CH_4 emitted (0.88 MT CO_2 eq.) and to 1.36 kt of N_2O emitted. (0.41 MT CO_2 eq.).

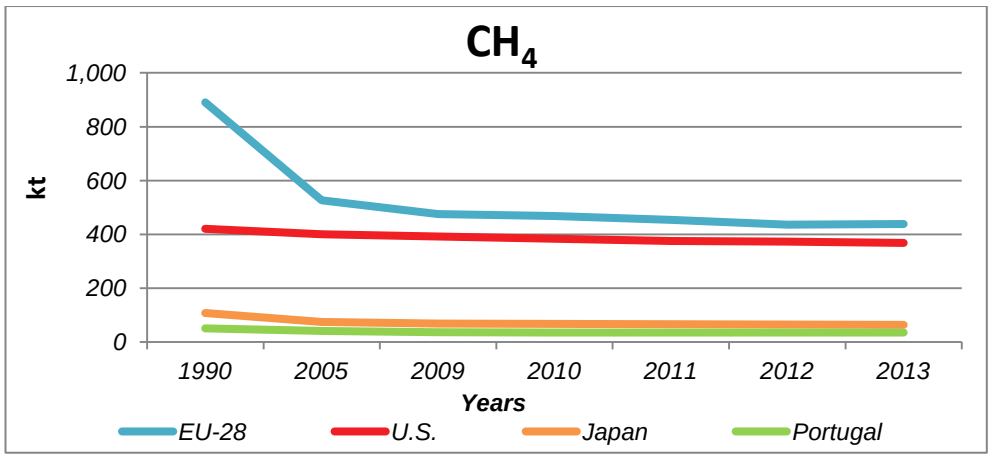

Figure 5 – Methane emission from domestic WWTPs, of Selected Countries. (Appendix I, Table 85) UNFCCC[3] [11][12]

[3] The most recent year for public inventory submissions of GHGs (from domestic WWTPs) by UNFCCC is 2013.

N_2O emissions from domestic wastewater are from centralized wastewater treatment processes and from effluent that has been discharged into aquatic environments [11].

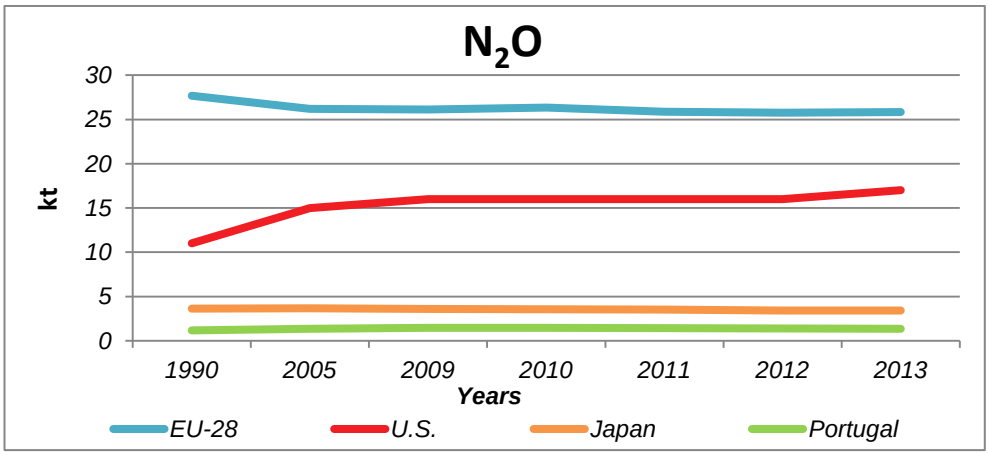

Figure 6 – Nitrous oxide emission from domestic WWTPs, of Selected Countries. (Appendix I, Table 87) UNFCCC [11][12]

Individual industrialized countries will have mandatory emissions targets they must meet. However, it is understood that some will do better than expected, coming in under their limits, while others will exceed them [10].

A coefficient that relates the activity data to the amount of chemical compound is named as emission factor, and is the source of later emissions [8]. Table 2 presents implied N_2O emission factor in 2013, from selected domestic WWTPs.

Table 2 – Implied N_2O Emission Factor, from selected domestic WWTPs, in 2013, expressed as g N_2O-N per kg sewage of N produced. UNFCCC [13]

N_2O Emission Factor	EU-28	U.S.	Japan	Portugal
g N_2O-N.(kg $N_{influent}$)$^{-1}$	5.7	5.0	5.0	9.98
Percentage	0.57 %	0.5 %	0.5 %	0.998 ≈ 1 %

As far as N_2O is concerned, the Intergovernmental Panel on Climate Change (IPCC, 2006) proposes an emission factor of 3.2 g N_2O-N.PE^{-1}, which amounts to 0.35 g N_2O-N.(kg $N_{influent}$)$^{-1}$ (0.035%) for developed countries [28]. This emission factor is based on a single study (Czepiel et al., 1995). However, the value from this study falls within the wide range of emission factors from previous studies:

0.001% - 14.6% of the in-coming nitrogen (Kampschreur et al., 2009)

0.01% - 1.8% of the in-coming nitrogen (Ahn et al., 2010)

0.06% - 25.3% of the in-coming nitrogen (Foley et al., 2010)

The wide variability between the normalized N_2O emissions, from different plants that were monitored, demonstrates the meaninglessness of the use of a single emission factor [28].

2.4 Schematic Overview of a Domestic WWTP

The non CO_2 greenhouse gases that can be emitted from a domestic wastewater treatment plant are N_2O and CH_4 (chapter 2.3). A schematic overview of the plant is presented in Figure 7, as well as, the locations where these gases can be emitted.

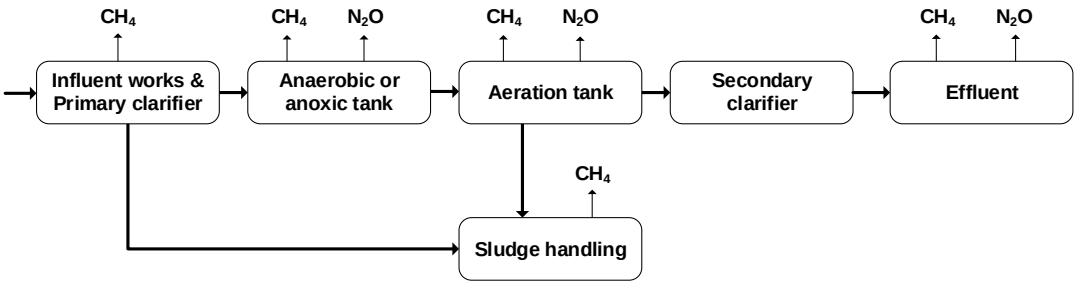

Figure 7 – Locations where CH_4 and N_2O can be emitted at a WWTP [14].

Methane that is emitted from the influent works is most likely formed in the sewer system, as the retention time of the wastewater in the influent works is too short to form CH_4. Furthermore, CH_4 formation will only occur where anaerobic[4] or anoxic[5] conditions prevail, as in the anaerobic or anoxic tank, but then only in the biofilms at the side of tanks, and at sludge handling sites. For this reason, no CH_4 formation is expected in an aeration tank. Methane that is emitted here is formed earlier and is stripped to the gas phase in the aeration tank [14].

Formation and emission of N_2O can only occur under anoxic or aerobic[6] conditions in the presence of nitrate (and carbon source) and ammonium [14]. Measurements at one WWTP, indicate that 90% of the N_2O emission occurs from the activated sludge compartments (where biological processes remain), 5% from the grit tanks (mechanically cleaning) and 5% from the sludge storage tanks (Czepiel et al. 1995). Nitrogen that is not converted leaves the WWTP via the effluent and can lead to the emission of N_2O from surface water.

2.5 Oxygen-depleting forms of Carbon and Nitrogen from Water

A major goal of biological wastewater treatment is removal of oxygen-depleting forms of carbon and nitrogen from water. These substances are routinely quantified in terms of the mass of oxygen required for complete oxidation [2].

[4] Microbes living without air (total absence of free oxygen (O_2) or bound oxygen (NO_2, NO_3)).
[5] Microbes living in the absence of free oxygen (O_2), but in the presence of bound oxygen (NO_2, NO_3)).
[6] Microbes living with air (total presence of free oxygen (O_2) or bound oxygen (NO_2, NO_3)).

Organic compounds are collectively quantified as Chemical Oxygen Demand (COD[7]). Reduced, oxygen-depleting forms of nitrogen (ammonia, organic nitrogen, and nitrite) are likewise quantified as Nitrogenous Oxygen Demand (NOD[8]). Theoretical Oxygen Demand (ThOD) is the sum of COD plus NOD. Many processes efficiently remove ThOD, but these processes differ dramatically in production and consumption of energy and in production of biosolids. The use of aerobic processes to remove biodegradable COD, for example, requires energy-intensive O_2 delivery and generates large quantities of biomass, but anaerobic processes remove COD for energy production and generate comparatively little biomass [2].

2.6 N_2O Generation in Domestic WWTPs

Nitrous oxide can be produced during the conversion of nitrogen compounds in WWTPs. The processes involved are nitrification and denitrification. Beyond that, there can also be N_2O generation when e.g. biogas[9] is burned at the WWTP for electricity production [14].

Nitrification

Nitrification is performed by three different groups of autotrophic microbes: Ammonium-oxidizing bacteria (AOB) and ammonium-oxidizing archaea (AOA), that convert ammonia into nitrite (NO_2^-); Nitrite-oxidizing bacteria (NOB), that convert nitrite into nitrate (NO_3^-) [14]. The different steps involved in the nitrification are presented in Figure 8.

AOB / AOA

$$NH_3 + O_2 + 2H^+ + 2e^- \longrightarrow NH_2OH + H_2O$$

$$NH_2OH + H_2O \longrightarrow NO_2^- + 5H^+ + 4e^-$$

$$0.5\ O_2 + 2H^+ + 2e^- \longrightarrow H_2O$$

Total $\quad \mathbf{NH_3 + 1.5\ O_2 \longrightarrow NO_2^- + H^+ + H_2O}$

NOB

$$NO_2^- + H_2O \longrightarrow NO_3^- + 2H^+ + 2e^-$$

$$0.5\ O_2 + 2H^+ + 2e^- \longrightarrow H_2O$$

Total $\quad \mathbf{NO_2^- + 0.5\ O_2 \longrightarrow NO_3^-}$

Figure 8 – Conversion steps in the nitrification process (Colliver, 2000).

[7] The mass of oxygen (O_2) required for stoichiometric oxidation of organic compounds to carbon dioxide (CO_2).
[8] The mass of oxygen (O_2) needed for stoichiometric oxidation of oxygen-depleting forms of nitrogen to nitrate (NO_3).
[9] Waste gas mixture (mainly CH_4 and CO_2, but it can also contain other impurities such as nitrogen or ammonia).

In WWTPs, nitrification is assumed to be predominantly performed by autotrophic AOB and NOB that use ammonia or nitrite as their energy source and CO_2 as carbon source [15]. Even though N_2O is not present as an intermediate in the main catabolic pathway of nitrification, AOB are known to produce N_2O since AOB contain as well the enzymes to reduce NO_2^- and NO, with N_2O as final product. These enzymes are the same as in regular denitrifying bacteria (DEN), but that in AOB denitrification is not associated with growth [14].

Ammonia oxidation can also be performed by heterotrophic bacteria, which, however, do not gain energy from this conversion. Pure culture studies indicate that heterotrophic nitrification can emit more N_2O than autotrophic nitrification [15].

Denitrification

Denitrification is performed by a diverse group of microorganisms, bacteria as well as archaea, which couple oxidation of organic or inorganic substrates to reduction of nitrate, nitrite, NO and N_2O. As N_2O is an intermediate in the denitrification process, incomplete denitrification can lead to N_2O emission. Many denitrifying microorganisms are facultative denitrifiers, which preferentially use oxygen as electron acceptor, due to the higher energy yield [14]. The different steps involved in the denitrification are presented in Figure 9.

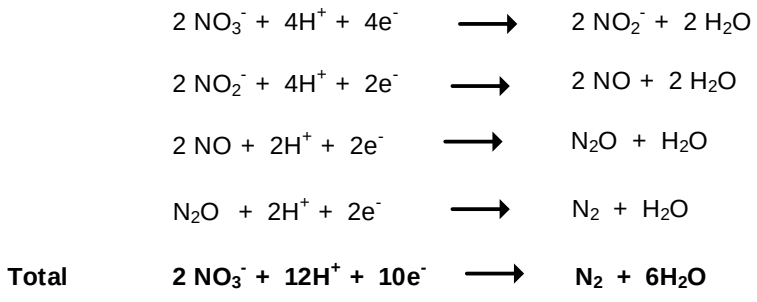

Figure 9 – Conversion steps in the denitrification process (Otte, 2000).

Some microorganisms can denitrify under both aerobic and anoxic conditions, a process known as aerobic denitrification (Robertson et al., 1995). Often these microorganisms can also catalyze heterotrophic nitrification (Robertson et al., 1989).

Also AOB can denitrify from nitrite to N_2O, with ammonium or hydrogen as the electron donor. This process is known as nitrifier denitrification (Bock et al., 1995).

Anaerobic ammonium oxidation bacteria (Anammox) can also denitrify, but do not use reduce nitrite through conventional denitrification via N_2O and consequently are not expected to emit N_2O. It's a particular type of denitrification, in which reduction of nitrite is coupled to ammonia oxidation (Kartal et al., 2007). A schematic overview is present in Figure 10.

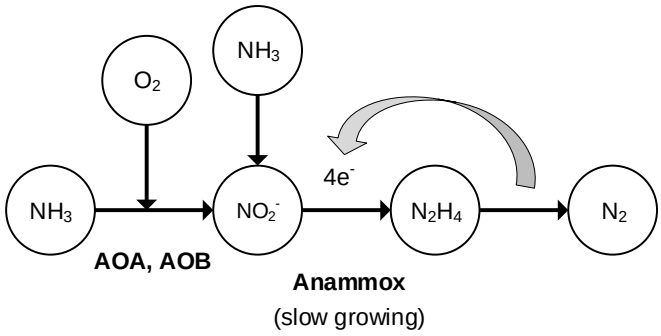

Figure 10 – Schematic illustration of a known technique for microbially processing nitrogen [1].

In other words, Anammox bacteria obtain reducing equivalents for reduction of NO_2^- to N_2 from the oxidation of NH_4^+ rather than COD, with hydrazine (N_2H_4) as a critical intermediate. By avoiding the use of COD as the source of reducing equivalents, more COD is available for recovery as CH_4 [16].

In wastewater treatment, it is generally agreed that anoxic heterotrophic denitrification is the dominant process, meaning that aerobic denitrification and nitrifier denitrification only play a minor role. Both aerobic denitrification and nitrifier denitrification seem to yield (relative to the N-converted) more N_2O than heterotrophic denitrification (Otte et al., 1996; Colliver and Stephenson, 2000).

Chemical Reactions

Possible chemical pathways leading to N_2O formation in WWTPs are the reaction between NO_2^- and NH_2OH leading to NO and N_2O, and nitrite reductions with organic or inorganic compounds. In the first reaction the intermediate NH_2OH production by AOB is required, complicating the distinction between chemical and biological N_2O production [14].

Schematic Overview of Biological Nitrogen Conversions

The relevant biological nitrogen processes are schematically presented in Figure 11. Complete nitrification comprises step 1 and 2; Complete denitrification step 3-6.

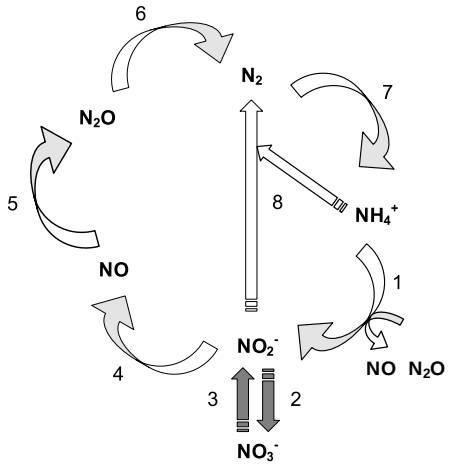

Figure 11 – Biological Nitrogen Conversions [15].

The biological steps in Figure 11 are synthesized in Table 3.

Table 3 – Biological Nitrogen Conversions [15].

Step	Biological Reactions
1	Aerobic ammonia oxidation (autotrophic and heterotrophic AOB and AOA)
2	Aerobic nitrite oxidation (NOB)
3	Nitrate reduction to nitrite (DEN)
4	Nitrite reduction to nitric oxide (AOB and DEN)
5	Nitric oxide reduction to nitrous oxide (AOB and DEN)
6	Nitrous oxide reduction to dinitrogen gas (DEN)
7	Nitrogen fixation (not relevant in most WWTPs)
8	Ammonium oxidation with nitrite to dinitrogen gas (Anammox)

2.7 Domestic WWTPs as Engineered Systems

The microbial nitrogen transformation processes in a wastewater treatment plant are fundamentally the same as in other environments such as soil, marine and freshwater habitats. However, unlike most other environments, wastewater treatment plants are engineered systems designed to achieve high nitrogen conversion rates [16]. There are several key features that distinguish these plants from other environments:

- Domestic wastewater usually contains relatively high concentrations of nitrogen, around 20 – 70 mg/L total nitrogen as N. In order to attain almost complete nitrogen removal within 3 – 8 h, high nitrogen loading rates are applied, incurring relatively high nitrification and denitrification rates. These are expected to impact on the rate of N_2O production [16].

- Bacterial communities in the plants are subjected to rapid changes in process conditions that are applied to promote aerobic or anoxic microbial reactions. Such rapid changes in environmental conditions probably cause physiological stress to both the nitrifying and denitrifying communities, with the potential to induce transient behaviours [16].

- Active aeration is used to induce aerobic conditions. The aeration systems are engineered to efficiently provide oxygen to the bioreactor, which also enables efficient transfer of N_2O from the liquid phase to the gas phase. Therefore, any temporary imbalance between N_2O production and consumption could result in accumulation and then stripping of N_2O during aeration [16].

- Activate sludge system is the most widely used form of secondary wastewater treatment. It refers to conversion of organic matter into CO_2, water, and other inorganic compounds, thus it can be appropriate where high removal of organic pollution is required. The process itself has flexibility and numerous modifications can be tailored to meet specific requirements (e.g. for nitrogen removal) [17].

Given that wastewater treatment systems are highly engineered systems, there are opportunities to mitigate N_2O emissions by improving process design and/or operational conditions [16].

2.8 Energy Consumption

A substantial disadvantage of the established methods for domestic wastewater purification is the higher energy consumption, which results chiefly from the high demand for delivery of air (or oxygen), for the oxidation reactions, and from the large quantities of wastewater that must be treated, transported, and as applicable heated, in wastewater treatment facilities [18]. Also, the operating costs of WWTPs in the recent years have increased substantially due to the increases in the unit cost of energy [19].

The net energy demand of treated wastewater can be expressed as Equation 2.

Net energy demand = *energy demand for aeration* **–** *energy recovered from biogas combustion*

+ *energy of baseline plant operation*

Equation 2 – Net energy demand for WWTPs [20].

2.9 Biogas Production

Anaerobic digestion is an established technology for the treatment of wastes and wastewater. It's a simple process, with a low energy requirement, used to convert organic material, such as solid wastes and biomass, into biogas [21]. The biogas product is typically composed of 50-75% methane and 25-50% carbon dioxide. Depending on the feedstock, biogas can also contain significant amounts of hydrogen sulphide, water and traces of other chemical products, which are presented in Table 4.

Table 4 – Typical composition of biogas from normally functioning digesters [22].

Compound	Chemical	Range %
Methane	CH_4	50 – 75
Carbon dioxide	CO_2	25 – 50
Nitrogen	N_2	0 – 10
Hydrogen	H_2	0.01 – 5
Oxygen	O_2	0.1 – 2
Water vapour	H_2O	0 – 10
Hydrogen sulphide	H_2S	10 – 30,000 ppm
Ammonia	NH_3	0.01 – 2.5 mg/m^3

Biogas can be utilised for the production of heat, co-generation of electricity and heat or for upgrading to natural gas or fuel gas quality [23]. In WWTPs, biogas most often is used for processing into electricity and/or heat. Recovered generator heat can be used to dry the remaining digester solid for plant fertilizer, which can be sold for additional revenue for the WWTP [24].

The amount of energy used for a plant operation ranges between 20 – 50% of the total biogas energy contents depending on climate and technical specifications [21]. Due to the efficiency of energy conversion processes, preferred are processes involving the purification of biogas [23].

Purification of biogas is mainly focused on the removal of hydrogen sulphide and water [23], to prevent corrosion of installed equipment or to achieve adequate quality standards for use. A general overview of biogas usage and biomethane production is present in Figure 12.

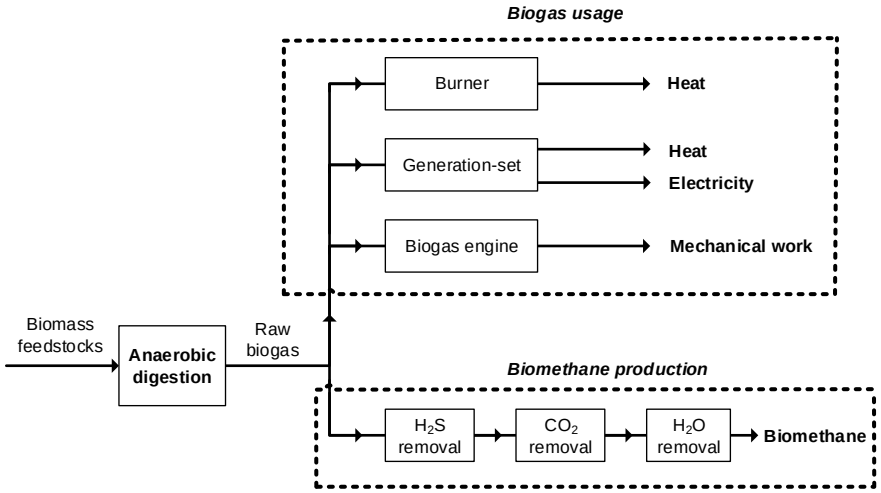

Figure 12 – Schematic diagram of biogas usage and biomethane production (CALSTART White Paper, 2010).

Environmental Protection Agency (EPA) concluded that WWTPs with influent flow rate less than 19,000 m^3/day didn't produce enough biogas, to make its use as a renewable source economically feasible. This problem limits the use of biogas (for the plant in-field sustainable power generation) from the point of WWTP scale [19].

2.10 N_2O as a Powerful Oxidant in Combustion Reactions

N_2O has a positive enthalpy of formation, releasing 82 kJ/mol when decomposed (Equation 3). Thermal decomposition of N_2O occurs at approximately 850ºC, but the presence of a transition metal oxide catalyst can enable self-sustaining decomposition and net energy production at decomposition temperatures as low as 300ºC.

$$\boldsymbol{N_2O \rightarrow \frac{1}{2}O_2 + N_2,} \qquad \boldsymbol{\Delta\widehat{H}_R^0 = -82\ kJ\ mol^{-1}}$$

Equation 3 – Decomposition of N_2O [2].

The energy released by decomposition of 1 mole of N_2O is approximately equivalent to the energy released by combustion of 0.1 mole of CH_4. When used to oxidize methane, N_2O increases the heat of reaction by -329 kJ/mol (Equation 4) as compared to O_2 (Equation 5).

$$\boldsymbol{CH_4 + 4N_2O \rightarrow CO_2 + 2H_2O_{(l)} + 4N_2,} \qquad \boldsymbol{\Delta\widehat{H}_R^0 = -1219\ kJ\ mol^{-1}}$$

Equation 4 – Combustion of CH_4 with N_2O [2].

$$\boldsymbol{CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O_{(l)},} \qquad \boldsymbol{\Delta\widehat{H}_R^0 = -890\ kJ\ mol^{-1}}$$

Equation 5 – Combustion of CH_4 with O_2 [2].

2.11 CANDO, a New Nitrogen Removal

Over the past two decades, European researchers have vastly improved treatment options for nitrogen removal using ecological "short-circuits" that avoid NO_3^- production. Examples include SHARON, OLAND, and CANON with Anammox. In these processes, NH_4^+ is only partially oxidized to NO_2^-, decreasing O_2 requirements, and NO_2^- is reduced to N_2 in three steps, rather than four, conserving COD for energy recovery as CH_4. This is achieved by implementing a correspondingly adapted process control system and by using alternative microorganisms. Treatment of anaerobic digester centrate with Anammox has the potential to decrease energy consumption of a full-scale plant by > 50% and increase CH_4 production by up to 25% [2].

Many processes recovery energy from waste COD as methane, but none recovers energy from NOD as nitrous oxide. A new nitrogen removal exploits the thermodynamic proprieties of N_2O (chapter 2.10) for energy recovery and is referred as Coupled Aerobic-Anoxic Nitrous Decomposition Operation (CANDO), which involves the following three steps:

I. Partial aerobic nitrification of NH_4^+ to NO_2^-
II. Partial anoxic denitrification of NO_2^- to N_2O
III. N_2O conversion to N_2 with energy recovery via catalytic decomposition of N_2O or use of N_2O as an oxidant of CH_4

Step I and III in CANDO have been demonstrated at full-scale. Step I is achieved with the SHARON process: partial oxidation of NH_4^+ to NO_2^-. Full-scale SHARON processes have reported over 95% nitrogen removal efficiency. Accordingly, bench-scale experiments focused on step 2 [2].

Table 5 compares oxygen requirements, biomass production and energy recovery for complete nitrification-denitrification ("nit-denit.") and three "short-circuit" nitrogen removal processes [2].

Table 5 – Theoretical upper bound for four N removal processes treating U.S *per capita* nitrogen and BOD_L[10] (Annex I, notes/assumptions).

Process	SRT denit. (days)	f_s^0 denit.[11]	Oxygen (g day^{-1})	Biomass (gCOD day^{-1})	Energy (MJ day^{-1})
Complete nit.-denit.	5	0.58	48	37	1.06
SHARON	5	0.58	37	27	1.36
CANON (Anammox)	60	0.14	21	13	1.78
CANDO	5	0.58	38	22	1.56[12]

[10] Loads of 13.3 g-N (nitrogen) and 142 g-BOD_L, per day, respectively.
[11] f_s^0 is defined as the maximum biomass yield expressed in dimensionless units.
[12] Recovery energy from CANDO is derived from COD (as CH_4) and NOD (as N_2O).

The CANON process with Anammox (slow growing bacteria) has the highest theoretical energy recovery, the lowest O_2 requirements, and the lowest biomass production. This is followed by CANDO, which generates a smaller energy surplus because more oxygen is required for partial-nitrification and more COD is consumed for partial-denitrification [20].

If CANDO can be scaled up and its efficiency improved, or another N_2O-producing strategy developed, CANDO would be an attractive option in terms of footprint for nitrogen removal [2]. This process mitigates the release of N_2O to the atmosphere [2] and relies upon faster growing heterotrophic organisms, decreasing solids residence time and enabling more rapid start-up and recovery from disturbances [20].

2.12 Maximizing N_2O production, in WWTPs: Risks and Safety

From previous literature review, two substantial problems are identified, at WWTPs:

I. Higher energy consumption leading to increased operating costs, due to the increases in the unit cost of energy (chapter 2.8);

II. N_2O is a generated by-product, and it may leave via the effluent if reduction to N_2 is incomplete (chapter 2.4). Enabling its emission into the atmosphere, N_2O can contribute to the greenhouse effect and consequently to global climate change (chapter 2.2).

As researchers have never attempted to maximize N_2O production rates, but have instead focused on minimizing or eliminating N_2O production in WWTPs [1], then if N_2O gas is recovered and purified in WWTPs, a chance to have this by-product recognized as a saving potential may be possible:

- ✓ If N_2O production is maximized in WWTPs, a chance to convert WWTPs into higher energy generators may be possible. N_2O increases the energy recovered in combustion reactions, as compared to conventional process which uses O_2 to oxidize CH_4, at WWTPs (chapter 2.10).

- ✓ If N_2O production is maximized in WWTPs, a chance to convert WWTPs into a business company also may be possible, using N_2O as the selling product. N_2O is commonly used to supercharge the engines of high performance vehicles (i.e. *Nitrox*) and as an oxidant in hybrid rocket motors in the aerospace industry [2].

As such, both options may mitigate the release of N_2O to the atmosphere, through its recovery from wastewater to the gas phase. However, there are some points that necessary need to be focused on the maximization process, concerning its risks and hazards to the environment. Safety strategies must be taken for instance.

N_2O From the Liquid Phase to the Gas Phase

In WWTPs, producing N_2O in large quantities may cause a great formation of N_2O in the liquid phase, as in the activated sludge compartments where biological processes remain. Even though there's a relatively high solubility of N_2O in water (1.08 g/L at 25ºC, 1 atm [1]), if N_2O is subjected to active aeration then enables the efficient transfer of N_2O from the liquid phase to the gas phase, due to turbulences in water. In order to make sure that all N_2O formed is stripped to the gas phase, accurate control measurements (e.g. N_2O microsensors), in situ, must be taken to prevent N_2O escaping via the effluent.

Infrastructures

In order to N_2O gas be captured some kind of campanula must exist, and between it and the biological tank(s) a pressured zone is created, allowing the N_2O gas to be pulled in a particular direction. It should be similar to the way biogas is removed from sludge digesters, at WWTPs.

The biogas zone areas are classified as ATEX zones (explosives atmospheres[13]), since CH_4 is highly flammable, and therefore are associated with assured local safety conditions. N_2O is a non-flammable gas [42] so there is no major risks of explosion. However, N_2O capturing zone area may also be associated with assured local safety conditions, to prevent possible gas dispersion out of the capturing environment for instance.

In case the biological tank(s) are open air zones then handling infrastructures to cover the entire N_2O capturing zone area, should be required. N_2O gas can't be allowed to escape, except via the suction tube (e.g. campanula). In other words, there must only be one exit in which N_2O gas goes through.

[13] Air mixtures with flammable substances (gases, vapors or dusts), in which, after ignition, combustion spreads to the entire unburned mixture.

2.13 Domestic WWTPs as Potential Sources of N_2O

In WWTPs the release of N_2O from biological nitrogen removal processes has been identified to be particularly influenced by the DO concentration and rapidly changing oxygenation conditions – i.e. periodical switch between anoxic and oxic conditions (Chandran et al., 2011). It has been observed that a low concentration in the aerated zones may enhance N_2O production throughout the nitrifier denitrification pathway. At the same time, too high aeration rates in the nitrification tank may lead to an increased oxygen introduction to the denitrification tank and lead to incomplete heterotrophic denitrification with enhanced N_2O emissions (Ahn et al., 2010, Kampschreur et al., 2009).

The main parameters leading to N_2O emission are schematically presented in Figure 13.

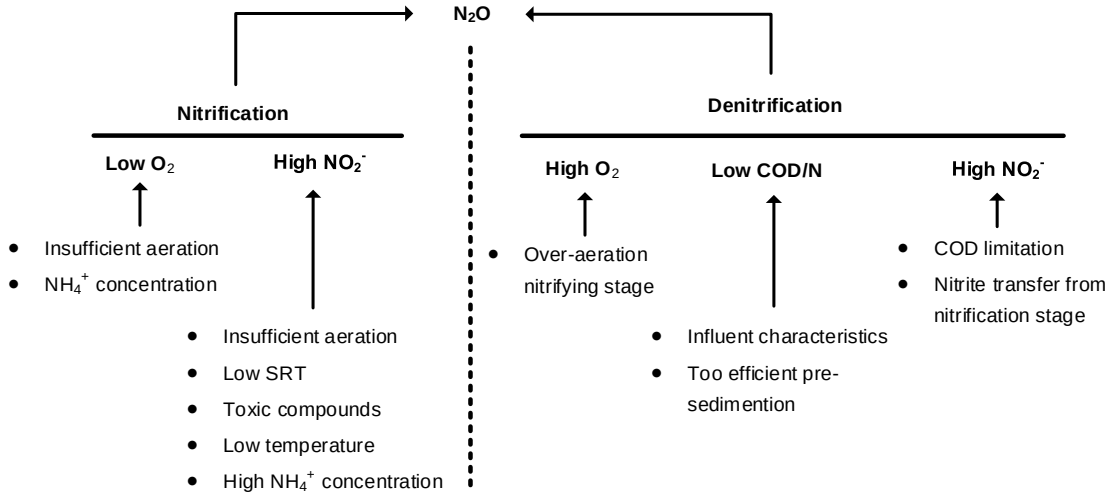

Figure 13 – Main process parameters leading to N_2O formation and emission [14].

Within this context, the following aeration strategies will aim at comparing N_2O emission patterns.

2.13.1 Potential of Aeration Control: the impact of N-removal over Nitrite

At a bench-scale experiment, a study (from literature) investigated the potential of aeration control for the achievement of N-removal. The flocculent sludge used for inoculation was provided by the WWTP Thunersee (Switzerland), which treats N and P biologically in a continuous anaerobic-anoxic-aerobic process.

Granular sludge with N-removal over nitrite (NO_2^-) and nitrate (NO_3^-), respectively, was maintained in two SBRs. Conventional microbial nitrogen removal is carried out via-nitrate (chapter 2.6).

For both sludge types, N_2O was measured with two different aeration strategies: constant DO of 30% and intermittent aeration, and with two different influent COD concentrations: 400 and 600 mg COD/L.

The N_2O emissions varied between 0.7% and 12.9% of the influent N load under different conditions tested (Table 6). The highest N_2O emission of 12.9% was observed with constant DO, N-removal over nitrite and influent COD concentration of 400 mg COD/L, whereas the lowest emission of 0.7% was found with N-removal over nitrate and intermittent aeration. Increased COD concentrations had a decreasing effect on N_2O emissions under almost all conditions tested.

Table 6 – N_2O emissions with N-removal over nitrite and nitrate, respectively, with intermittent aeration and constant DO of 30% [26].

Aeration Strategy	COD concentration (mg COD/L)	Nitrite Pathway (% of N load) [14]	Nitrate Pathway (% of N load) [14]
Intermittent aeration	400	5.2 ± 1.1	0.8 ± 0.2
Intermittent aeration	600	2.4 ± 0.8	0.7 ± 0.3
Constant aeration	**400**	**12.9 ± 2.1**	**9.3 ± 2.4**
Constant aeration	600	8.1 ± 1.7	5.9 ± 0.9

The following shown profiles (Figures 14, 15, 16 and 17) represent typical profiles of N_2O concentrations in the effluent gas and the bulk liquid, during a SBR cycle. These profiles have been measured with 400 mg COD/L influent concentration. The dashed lines show schematically the aeration strategy.

With N-removal over nitrite and intermittent aeration (Figure 14) N_2O was only emitted during the aeration pulses. However, in the bulk liquid the concentration sharply increased right at the end of the aeration phase. Except for the first aeration pulse, two peaks of N_2O emissions were measured during each aeration pulse, one at the beginning and one at the end.

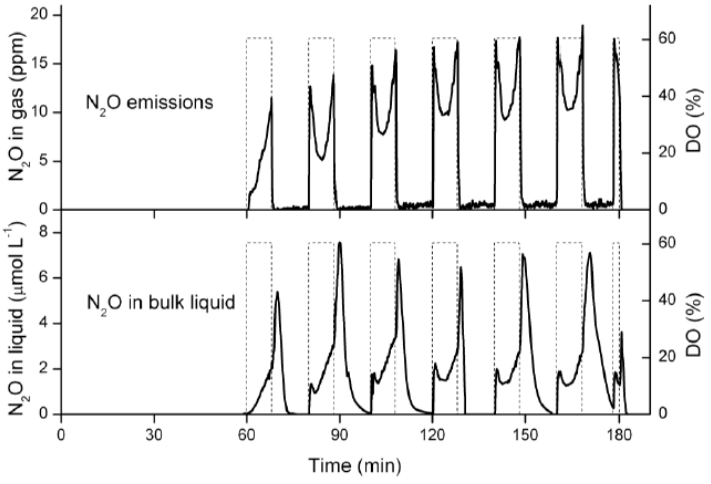

Figure 14 – N-removal over nitrite, with intermittent aeration [26].

[14] Part of nitrogen load leaving the reactor as N_2O gas.

Similar profiles for N_2O emissions and liquid concentrations were observed with N-removal over nitrate (Figure 15). However, the concentrations were lower than for N-removal over nitrite. Moreover, with N-removal over nitrate a small peak of N_2O appeared in the liquid phase during the first minutes of the feeding phase (Figure 15).

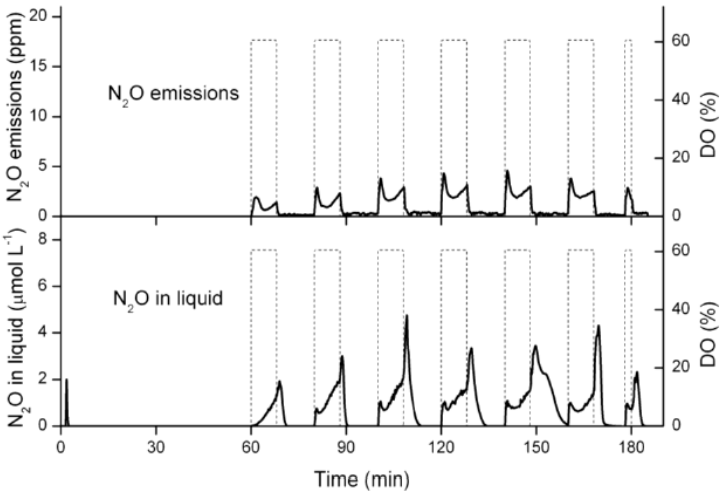

Figure 15 – N-removal over nitrate, with intermittent aeration [26].

With a constant DO of 30% and N-removal over nitrite, N_2O concentrations in the gas and the liquid phase constantly increased during the first minutes of the aeration, before reaching a steady state (Figure 16).

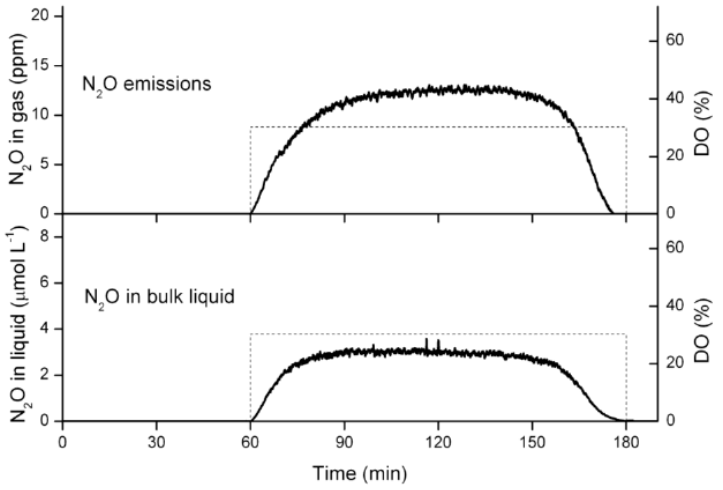

Figure 16 – N-removal over nitrite, with constant DO of 30% [26].

With N-removal over nitrate, the N_2O concentrations were again a bit lower (Figure 17). Also with constant DO a peak of N_2O in the liquid phase was observed during first minutes of the feeding phase and in the gas phase right after the aeration start (Figure 17). With N-removal over nitrite, these peaks didn't appear.

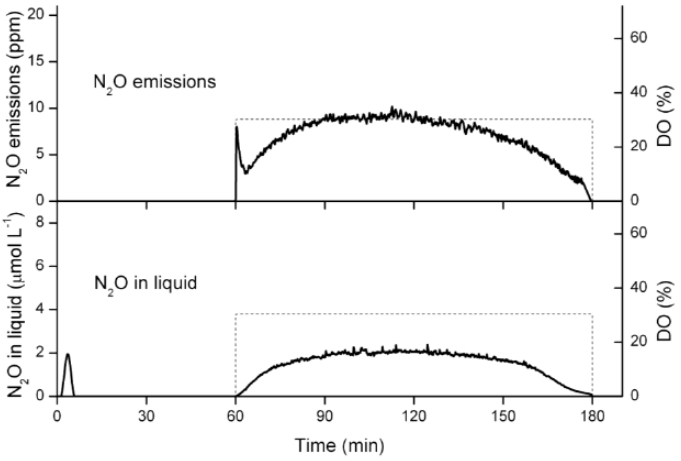

Figure 17 – N-removal over nitrate, with constant DO of 30% [26].

N_2O emissions were higher with N-removal over nitrite than over nitrate under all four tested conditions. From a mass balance perspective this does not compromise the advantages of N-removal over nitrite compared to N-removal over nitrate, since the difference in N_2O emissions were only in the order of 2% – 5% [26].

Moreover, N_2O emissions were lower with intermittent aeration than with a constant DO of 30% and overall the applied strategy with intermittent aeration and N-removal over nitrite resulted in lower N_2O emissions than classical N-removal over nitrate with constant aeration. Low DO concentrations enhance the production of N_2O [26].

With intermittent aeration the DO was either high or oxygen was completely absent. The reason for the N_2O peak right after aeration stop was most likely the remaining oxygen during the first 1 – 2 min after aeration stop. Simultaneous nitrification-denitrification could still occur, but the N_2O produced by these processes was not stripped anymore by the aeration. This N_2O was only removed from the reactor at the beginning of the subsequent aeration pulse, explaining the emission peak right after the start of aeration [26].

With N-removal over nitrate, a N_2O peak was observed during the first minutes of the feeding phase. This peak was most likely due to heterotrophic denitrification, and the emission peak due to the stripping of this N_2O. With N-removal over nitrite, almost no nitrite remained at the end of SBR cycle and therefore no heterotrophic denitrification took place during the subsequent feeding phase [26].

The DO signal appeared to be a valid and reliable criterion for the aeration phase length control. Aeration phase length control combined with intermittent aeration, or alternative high-low DO, is an efficient way to achieve N-removal over nitrite, which is especially interesting for COD-limited systems. N-removal efficiencies of up to 95% were achieved with this way of reactor operation [26].

2.13.2 Potential Production of N_2O, at full-scale WWTPs

N_2O emissions from WWTPs vary substantially between plants, probably because of different designs and operational conditions [16]. In order to check the potential of higher emissions of N_2O from different full-scale WWTPs, the following case studies are presented from literature.

Spain

- **<u>WWTP of La Roca de Vallès</u>**

A continuous on-line quantification of N_2O emissions from a full-scale sequencing batch reactor was performed in a study. The monitoring site was the municipal WWTP of La Roca de Vallès (Barcelona, Spain) which treats the domestic wastewater of 48,000 population equivalents. Different cycle configurations were implemented in the SBR aiming at reaching acceptable effluent values. Each cycle configuration consisted of sequences of aerated and non-aerated phases of different time length. Cycles with long aerated phases showed the largest N_2O emissions. N_2O cycle profiles, for each of the cycle configurations, measured in February, 2014, are presented in the gas and liquid phases, in Figures 18 and 19, respectively.

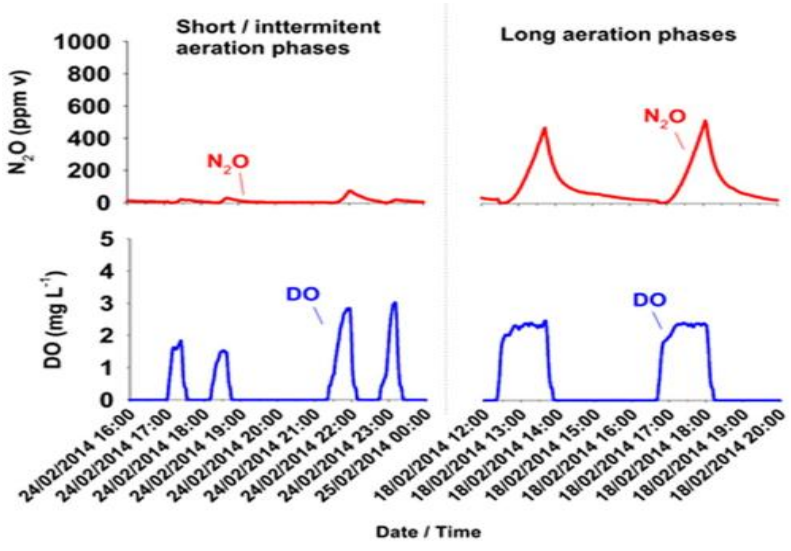

Figure 18 – Representative profiles of N_2O emission rates, in the gas phase, measured at a full-scale domestic WWTP, located in Spain (La Roca de Vallès) [27].

The measured dissolved N_2O and dissolved O_2 corresponds to grey and black lines, respectively (Figure 19).

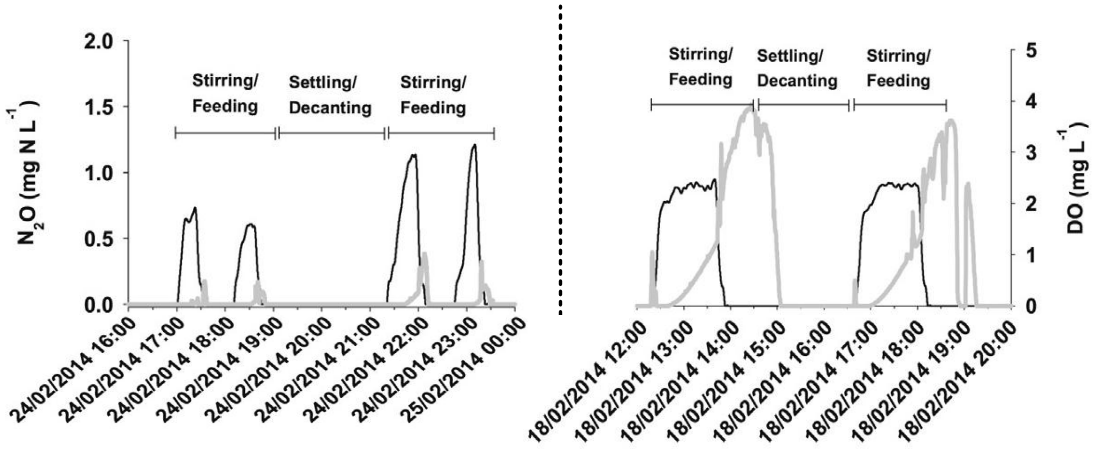

Figure 19 – Representative profiles of N_2O emission rates, in the liquid phase, measured at a full-scale domestic WWTP, located in Spain (La Roca de Vallès) [27].

In general, N_2O emissions at this plant were 97.1 ± 6.9 g N_2O – N/Kg NH_4^+ – N consumed (6.8% of the influent NH_4^+ – N load) [27]. This value is much higher than the one proposed by IPCC (chapter 2.3).

- **<u>WWTP of Granollers</u>**

Another case study was at a full-scale activated sludge bioreactor of the city of Granollers, near Barcelona (Spain). This plant treats the domestic wastewater of 112,000 population equivalents. After primary treatment and settling, the wastewater is treated biologically in two parallel and identical plug-flow reactors where COD and nitrogen removal is performed.

Dynamics of (**A**) N_2O (grey line), NH_4^+ (Δ), NO_2^- (•) and NO_3^- (▪) and (**B**) aeration flow (grey line) and DO (black line) during a period of nitrification instability, measured in June, 2013, are presented in Figure 20.

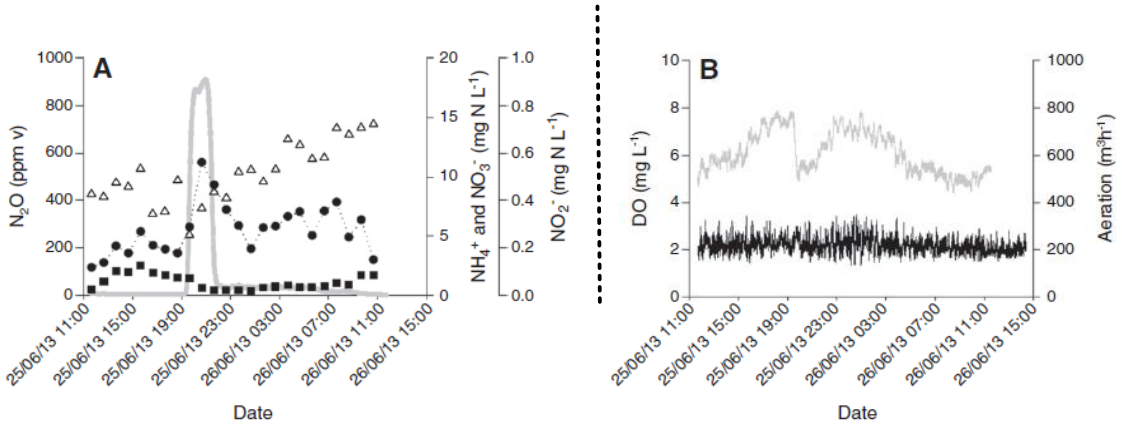

Figure 20 – Dynamics of (A) N_2O emission rate (grey line) and (B) aeration flow rate, measured at a full-scale domestic WWTP, located in Spain (Granollers) [29].

In general, N_2O emissions at this plant accounted for 0.116% of the total incoming nitrogen [29].

The high variability of N_2O emissions contributes to the hypothesis of N_2O production being strongly bounded to process configurations, performance or events.

- **WWTP of Catalonia**

N_2O emissions were also monitored in a municipal WWTP located in Catalonia (Spain), which was performing full partial nitrification of reject wastewater. The study was conducted in a SBR operation which resulted in a substantial increase on N_2O emissions.

Dynamics of (**A**) pH (grey line), DO (black line), ammonium (discontinuous line) and nitrite (□) concentrations, and (**B**) N_2O (black line), CH_4 (grey line) emission profiles, and aeration flow (discontinuous line) are presented in Figure 21.

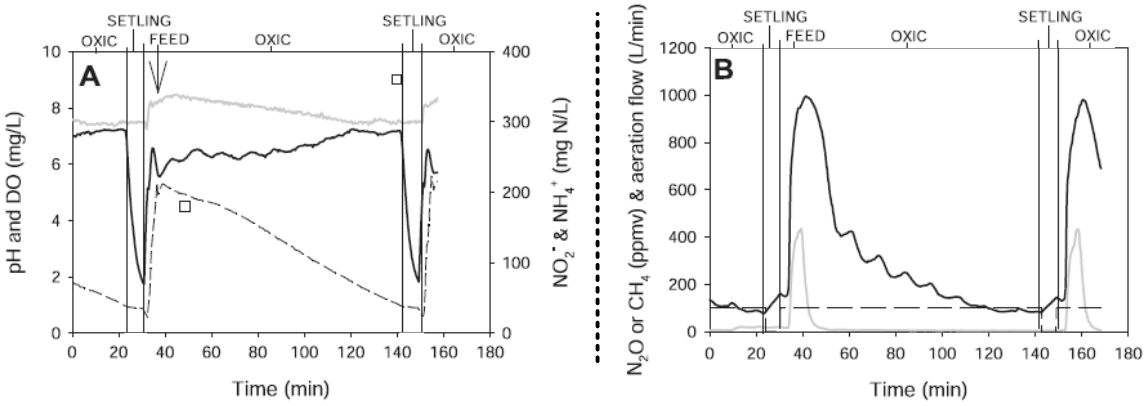

Figure 21 – Cycle study profile measured at a municipal WWTP (Catalonia, Spain) operating in SBR mode, with a settling time of 7 min and an aeration flow of 100 L/min [30].

Dynamic process conditions can enhance N_2O production, which was found to be dependent on dissolved oxygen concentration, increasing when reducing the DO values. N_2O emissions increased one order of magnitude reaching values of 19.3 $\pm$ 7.5% of the N oxidized [30].

Netherlands

- **WWTP of Olburgen**

A monitoring campaign of N_2O emission was conducted at a partial nitritation-anammox granular sludge reactor of the Olburgen sewage treatment plant (Netherlands), measured in August, 2011. The dynamic behavior during prolonged aeration after non aeration is presented in Figure 22.

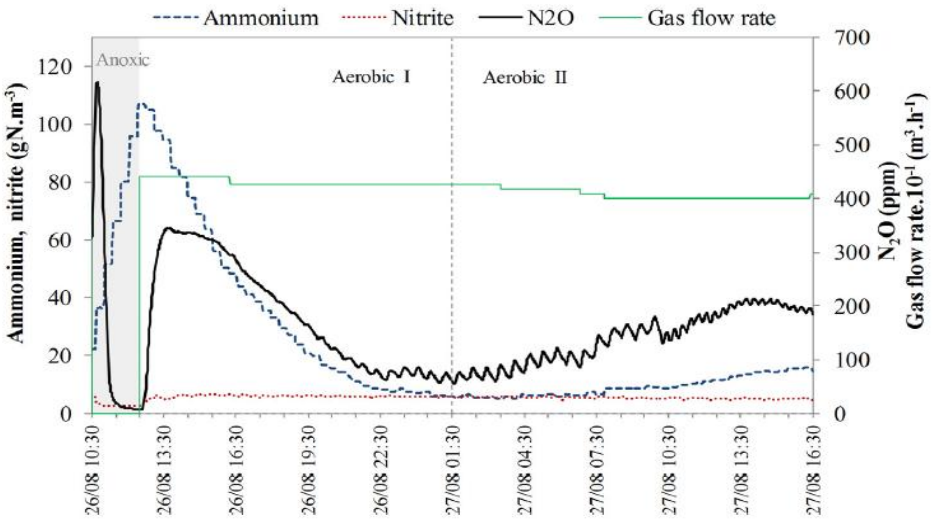

Figure 22 – Concentration profiles of N_2O (gas phase), ammonium and nitrite (liquid phase) and aeration gas flow measured at a full-scale granular sludge reactor, located in Olburgen (Netherlands) [31].

Evidence is available that aerated zones in WWTPs are prone to higher N_2O emissions compared to non-aerated zones or anoxic conditions (Ahn et al, 2010a, 2010b). The transient from anoxic to aerobic conditions as well as the accumulation or unlimited availability of ammonium was correlated to N_2O formation in other studies (Ahn et al., 2010 b; Chandran et al., 2011; Yu et al., 2010). Law et al. (2012b) reported a positive correlation between ammonium oxidation rate and N_2O formation, attributing the N_2O formation to the hydroxylamine route.

The mean (gaseous) N_2O-N emission obtained was 2.0% of the total incoming nitrogen during normal reactor operation [31].

- **WWTP of Rotterdam**

Another case study of N_2O formation was performed on a full-scale partial nitritation (SHARON) reactor, measured in July, 2010, in Rotterdam (Netherlands). This reactor is part of the sludge handling facility and treats the anaerobic digestion reject water.

Dynamics of (**A**) N_2O profile during aeration and non-aeration is shown by solid red line and blue dash-dotted line, respectively. Estimated aerobic N_2O formation is shown by green dotted line. Dynamics of (**B**) represent gas stripping device gas phase N_2O concentration and corresponding liquid phase N_2O concentration. Dynamics of (**C**) represent DO and pH profiles. The aeration on and off switch are shown by a dashed pink and solid black, respectively. Measurement results are presented in Figure 23.

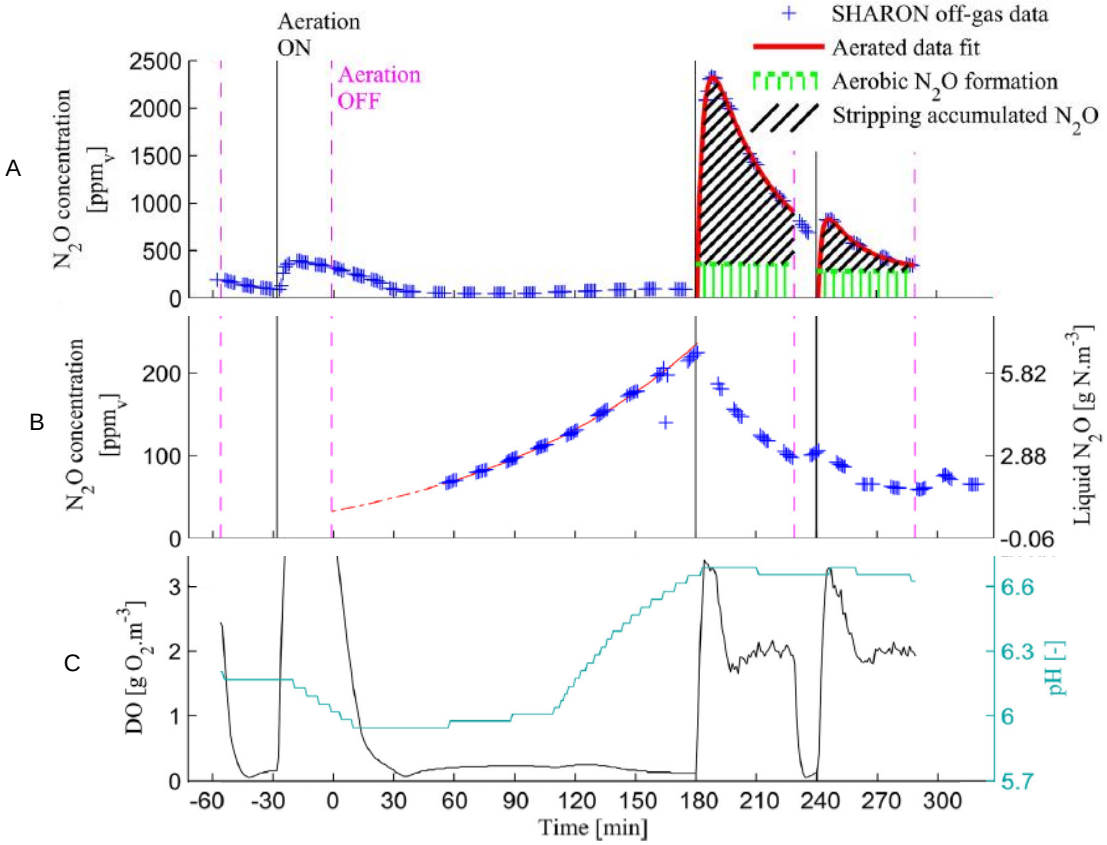

Figure 23 – N_2O emission from a full-scale partial nitritation SHARON reactor, located in Rotterdam (Netherlands) [32].

Under standard operation, 70% of the N_2O emission was attributed to anoxic N_2O formation. The overall N_2O emission was 3.7% of the incoming ammonium load [32].

Sweden

- **WWTP of Sjölunda**

A full-scale sludge liquor treatment plant at Sjölunda WWTP (315,000 population equivalents), in Malmö (Sweden), is operated with nitritation alone, which is highly enriched with aerobic AOB. The sludge liquor, originating from the dewatering of anaerobic digested sludge, is treated in a sequencing batch reactor (SBR). The treatment results in extremely high nitrite concentrations (600-850 mg NO_2-N/L) at low pH (6.8) and low DO concentration (1.3 mg/L) [33].

Online measurements were performed on the off-gas from the SBRs, in 2010. Concentrations and levels measured are presented in Figure 24.

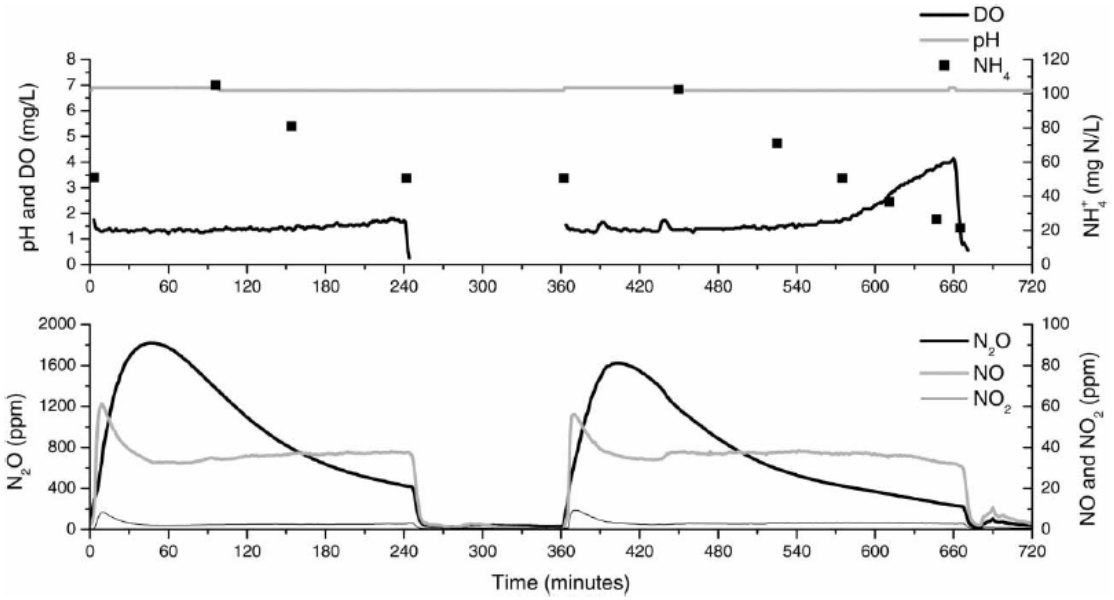

Figure 24 – Two consecutive SBR cycles showing DO and NH_4^+-N concentrations, pH and levels of N_2O, NO and NO_2 in the off-gas, at a full-scale sludge liquor treatment plant, located in Sjölunda (Malmö, Sweden) [33].

During normal operation, emissions of N_2O, NO and NO_2 were found to be 3.8%, 0.06% and 0.01%, respectively, of the ammonium nitrogen load [33]. The N_2O emissions correlated positively with the length of the previous anoxic period, i.e., settling and decantation, and with the ammonium oxidation rate.

2.14 N_2O Production via SNDPR Systems

Simultaneous nitrification, denitrification and phosphorus removal (SNDPR) has been proposed as an economically feasible process for wastewater treatment plants (Zeng et al., 2003b).

The presence of denitrifying glycogen-accumulating organisms (DGAOs) and the accumulation of N_2O can severely compromise the advantage of this process from a greenhouse gas emissions perspective [25]. DGAOs are mainly responsible for the denitrification activity rather than denitrifying polyphosphate-accumulating organisms (DPAOs). From a recovery perspective, SNDPR processes can represent an attractive method to maximize N_2O production from activated sludge systems.

The following systems are lab-scale studies, from literature, in which sludge from the Caboolture Sewage Treatment Plant (Queensland, Australia) is seeded into a sequencing batch reactor (SBR) and prepared synthetic wastewater is pumped into the reactor. In Table 7, the N_2O production is summarized, for nitrite (NO_2^-) and/or nitrate (NO_3^-) cycles.

Table 7 – N_2O Production via SBR systems.

Lab-scale Study	N_2O Production	SBR System
Case 1 [25]	**51 % (via NO_3^- and NO_2^-)**	**SNDPR**
Case 2 [34]	**64 % (via NO_2^-)**	**SNDPR**
Case 3 [35]	**90% (via NO_3^-)** **96 % (via NO_2^-)**	**Enrichment of DGAOs**

Ideally, the third case would be the best way of producing N_2O since a value between 90%-96% of the incoming nitrogen could be converted to N_2O (Table 7). However, this case represented an enrichment of DGAOs with limited biodiversity as compared to what would be typically expected in WWTPs, thus is not very representative of what would be achievable in a full-scale activated sludge system.

The SNDPR studies of Cases 1 and 2 contain a much higher biodiversity, including nitrifiers, ordinary heterotrophs, DPAOs and DGAOs, thus a value between 51%-64% of incoming nitrogen can reasonably be obtained for the production of N_2O via SNDPR system. In fact, the first case can possibly be an appropriate case scenario of producing N_2O, since nitrate is most often the dominant end product of nitrification in WWTPs, and also accounting that not all nitrogen compounds (e.g. organic N) are completely converted to ammonia followed by nitrite/nitrate in biological tank(s) of the full-scale plants.

2.15 The N_2O Market

The industrial gas industry has seen many changes in the last century. More gas is being required to keep up with technological demands, more countries are using gas for various purposes, advancing healthcare practices and the increasing aging population necessitate additional gas, and new industry lends itself to new applications of gas use [36].

Users of N_2O

Approximately 90% of the N_2O produced by the major manufacturing companies is used in health settings. Most of this amount (80%) is used by hospitals to facilitate general anesthesia. The field of dentistry uses up to 10% of the N_2O in ambulatory clinics [36].

The food industry uses approximately 5% to 8% of the N_2O manufactured. N_2O acts as a propellant for dairy products such as whipped cream in which N_2O is dissolved until it vaporizes with ambient air when expelled from the can. N_2O produces a whipped cream that is four times the volume of the liquid. N_2O is lipophilic, thus inhibiting degradation of the fatty cream, whereas if pressurized air was used, the oxygen would cause the cream to become rancid. N_2O has also been used to displace the oxygen in packages of foods such as potato chips to prolong freshness and prevent crushing [36].

In the semiconductor manufacturing industry, N_2O is employed as a chemical vapor deposition (CVD) process gas for depositing films. The use of a highly pure material (99.999%) is important in order to ensure uniform film growth during deposition [37]. In the information technology industry, N_2O oxidizes chemicals during the manufacture of computer chips, requiring also a highly pure N_2O [36].

The remaining users of N_2O include the chemical industry, in which N_2O is used in the production of sodium azide (NaN_3), the explosive agent that inflates an automobile air bag [36].

N_2O is also used to increase engine performance in the racing industry (i.e., cars, motorcycles, boats). Furthermore, N_2O can be used in a hybrid rocket engine as the oxidizer in combination with a fuel source, and in amateur and high-power rocketry [36].

N_2O consumption by different countries

Anesthesia/medical applications are the largest end-use market for N_2O, but they are growing the slowest. Aerosol propellants are the second-fastest growing mainly in Southeast Asia, although Western Europe is the largest consumer of N_2O in aerosol propellant applications. Nearly all of the N_2O used in semiconductor production is consumed in Japan, the Republic of Korea, Taiwan, the U.S., Singapore, Malaysia, China and Western Europe [38].

The pie chart presented, in Figure 25, shows world consumption of N_2O by different countries.

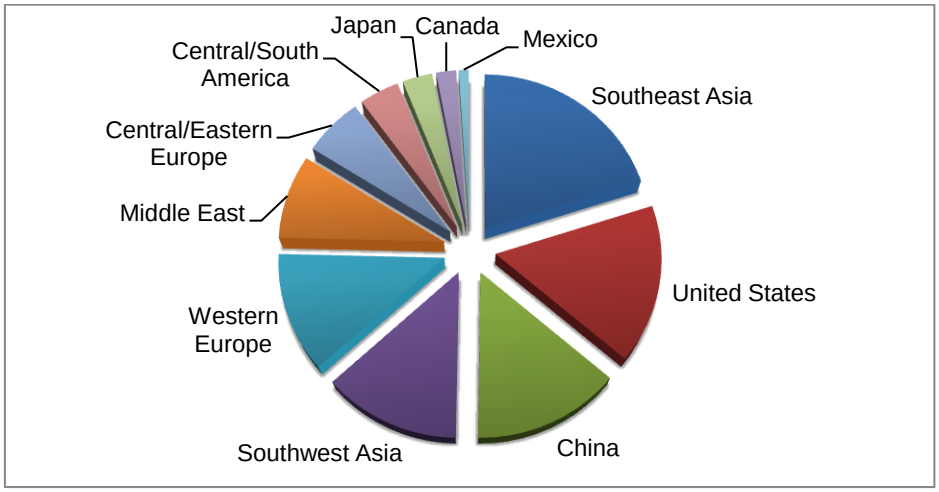

Figure 25 – Global N_2O Consumption, in 2010.
IHS Chemical [38]

Leaders of the Industrial Gas Industry

In 2013, the following four companies dominated the industry worldwide:

- Air Products and Chemicals, Inc. (U.S.)
- L'Air Liquide, S.A. (France)
- The Linde Group PLC (U.K.)
- Praxair, Inc. (U.S.)

Together, these companies supplied more than 60–70% of the industrial gas business [40].

In 2013, Linde introduced its new plant for the production of N_2O in Chungcheongnam, Korea. The plant has a production capacity of 3,000 tonnes per annum, enabling the Group to meet rising demand in that Asian country in both the rapidly growing electronics market and the health sector [41].

Chemistry of N_2O

N_2O is a non-flammable, colorless gas with a slightly sweet odor. It was discovered in 1772 and has been in common usage recreationally since the early 1800s [42].

Table 8 shows some physical gas proprieties of nitrous oxide.

Table 8 – Physical Gas Proprieties of N_2O [1] [42].

Systematic (IUPAC) name	Dinitrogen monoxide
Synonyms	Nitrogen oxide, laughing gas, hyponitrous acid anhydride, factitious air
Molecular Formula	N_2O
Molar Mass	44.01 g/mol
CAS Registry Number	10024-97-2
Melting Point	-90.81 ºC
Boiling Point	-88.46 ºC, 760 mmHg
Solubility	Relatively high solubility of N_2O in water (1.08 g/L at 25ºC, 1 atm); freely soluble in sulfuric acid; soluble in alcohol, ether, oils
Additional Data	Density 1.53 (Air = 1)
Notes	Very stable, rather inert chemically at room temperature

N_2O Manufacturing

The most common industrial process for the manufacture of N_2O is based upon thermal decomposition of ammonium nitrate (NH_4NO_3). There are a number of other N_2O production processes such as direct oxidation of ammonia or purification of off-gas (waste gas) from adipic acid production (polyamide chain) etc [43].

The pure NH_4NO_3 salt melts at 169ºC and begins decomposing at 190ºC. At temperatures up to 250ºC, exothermic and endothermic reactions can take place. The two predominate reactions are present in Equations 6 and 7, respectively. The decomposition reaction is the desired reaction [43].

$$NH_4NO_3 \rightarrow N_2O + 2H_2O \qquad \Delta\widehat{H}_R^0 = -59\ kJ\ mol^{-1}$$

Equation 6 – Decomposition of ammonium nitrate (exothermic reaction) [43].

$$NH_4NO_3 \rightarrow NH_3 + HNO_3 \qquad \Delta\widehat{H}_R^0 = +159.9\ kJ\ mol^{-1}$$

Equation 7 – Dissociation of ammonium nitrate (endothermic reaction) [43].

The dissociation reaction becomes appreciable at 210°C and continues to become more predominant with increasing temperature. Increasing pressure suppresses the dissociation reaction [43].

Therefore, the N2O byproduct obtained by this method is not pure. Some contaminants like ammonia (NH_3), nitric oxide (NO) and nitrogen dioxide (NO_2) are also formed [42].

N_2O Process and Storage

In Figure 26, a flowchart of the steps involved in manufacturing, repackaging and distributing N_2O is presented. These steps are summarized:

- The gas mixture is cooled to ambient room temperature, the steam is condensed, and most of the water is removed. The resulting crude N_2O gas mixture is scrubbed to extract the contaminants. The gas is compressed, dried to remove the remaining water, cooled, and liquefied. The resulting product is nearly pure (99.5% to 99.9%) and is stored as a liquefied, compressed gas at approximately 300 psi (21 bar) and 0º to 10ºF (-17.8º to -12.2ºC) in insulated and refrigerated storage tanks [36].

- The manufactured product is kept refrigerated until it is directly transferred by insulated tanker trucks to hospitals with their own large storage facilities or to other gas repackagers and distributors. The overall medical marketing and distribution system is very effectively and efficiently deployed in the industry [36].

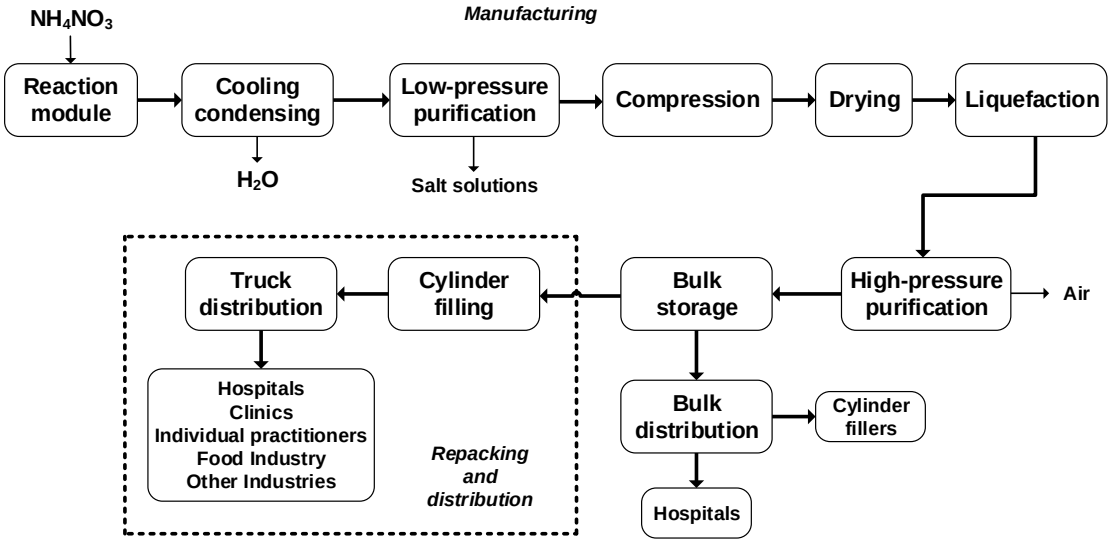

Figure 26 – Manufacturing, repackaging and distributing N_2O [36].

N_2O is also produced in large volumes as a by-product in the synthesis of adipic acid, one of the two reactants used in nylon manufacture [44]. A schematic overview of the production is presented in Figure 27.

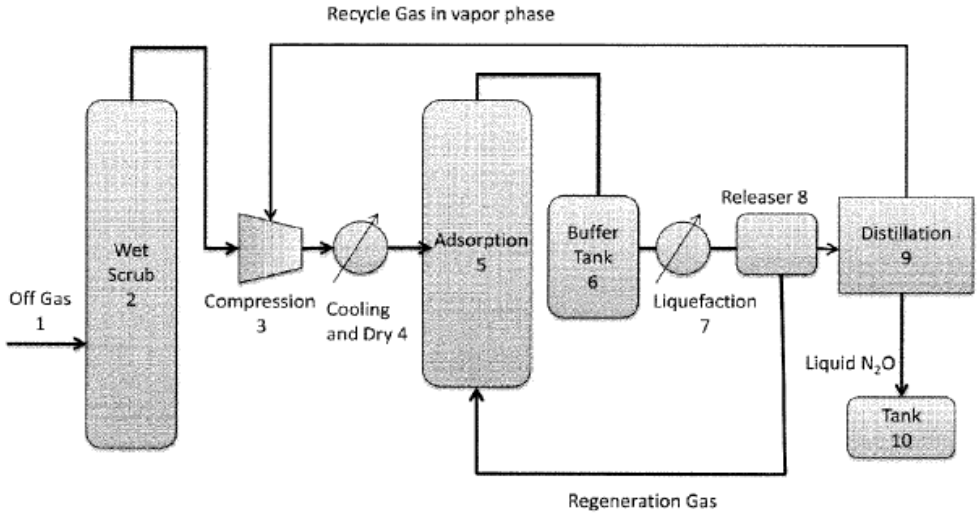

Figure 27 – Process for Recovery and Purification of N_2O, with Wet Scrubbing [44].
U.S. Patent 2014/0366576 A1 (Annex II, Figures 53 and 54)

3. Case Study of N_2O Purification

A full-scale WWTP not only brings the potential of N_2O production (chapter 2.13) but also requires energy and chemicals during the process. Energy consumption for wastewater treatment is a matter of concern on a microeconomic scale (chapter 2.8) and saving potentials need to be explored. Combining the possibility of wastewater treatment with fuel production (CH_4) associated to GHG reduction (N_2O recovery) opens a new dimension in water cycle, and really represents the key terms of sustainably and circular economy.

This study is now going to focus on the possibility of N_2O gas purification in a particular WWTP, located in Alcântara (Portugal). Three case scenarios will be evaluated in order to find out whether are appropriated and attractive in terms of production costs (economically feasible).

3.1 Fate of Gases Produced Through Denitrification

Although five gases are produced during denitrification, only three gases escape to the atmosphere from the wastewater (Table 9). The majority of gases that are produced consists of molecular nitrogen and carbon dioxide. Often, these gases alone with nitrous oxide become entrapped in floc particles and contribute to settleability problems in the secondary clarifier and thickener before the gases escape to the atmosphere.

Table 9 – Fate of Gases Produced Through Denitrification [45].

Gas	Formula	Fate
Molecular nitrogen	N_2	Insoluble in wastewater; Leaves as escaping bubbles.
Carbon dioxide	CO_2	Although soluble in wastewater, forms carbonic acid/bicarbonate alkalinity; Some leaves as escaping bubbles.
Nitrous oxide	N_2O	Insoluble in wastewater; Leaves as escaping bubbles.
Ammonia	NH_3	Converted to NH_4^+ at pH values < 9.4; NH_4^+ dissolves in wastewater.
Nitric oxide	NO	Not usually released from bacterial cell; Does not accumulate.

Part of the oxygen present in the aeration air will have been consumed[15] during its upward passage through the mixed liquor, and this will largely have been replaced by the carbon dioxide formed in the respiration process. As for nitrogen gas, this represents 78% of the atmospheric air [46].

[15] O_2 consumption typically from 21 to 18%

Therefore, an estimated steady state during denitrification can be obtained and is presented in Table 10. The corresponding 1% of N_2O gas may not be the accurate value since N_2O production can change depending on the WWTP specifications, but it is considered to be in the range typically observed at WWTPs, by Kampschreur et al. 2009, Ahn et al. 2010 and Foley et. al. 2010 (chapter 2.3).

Table 10 – Estimated Steady State, during denitrification.

Gases	In	Out
N_2	79%	78%
CO_2	-	3%
O_2	21%	18%
N_2O	-	1%
Total	**100%**	**100%**

3.2 Alcântara's WWTP (Portugal)

Alcântara's WWTP is responsible for handling urban wastewater of 800,000 population equivalents, mainly from Lisbon western zone, Amadora and Oeiras. After primary treatment and settling, the wastewater is treated biologically through the BIOSTYR technology, which involves a biofiltration system. The plant also has a deodorizing system with a capacity to treat 160,000 m3/h of polluted air. After biological treatment, the wastewater is disinfected by ultraviolet radiation and then the effluent goes toward the Tejo river, in environmentally safe conditions [47].

This plant features a unique covered configuration, in particular for its vegetation cover, favoring its landscaping and improving air quality, creating habitats and also promoting biodiversity in an urban context (Figure 28).

Figure 28 – Alcântara's WWTP, located in Lisbon (Portugal) [48].

In 2015, the average of Total Kjeldahl Nitrogen[16] (TKN) concentration of the plant's influent was 54 g N m^{-3} and the average of Total Nitrogen[17] (TN) of the plant's effluent was 29 g N m^{-3}. Also, the average of wastewater and escaping air flow rates was 7,327 m^3 h^{-1} and 7,038 m^3 h^{-1}, respectively. These reported values are from Alcântara's WWTP database.

Moreover, a monitoring campaign of N_2O was performed in Alcântara's WWTP, in 2015. It was registered an average of 570 kg N_2O-N per day (24 kg N_2O-N per hour), which was analysed using a published method (Marques et al. 2016), by colleagues at FCT/UNL.

N_2O emission factor can be calculated using Equation 8.

$$Emission\ factor\left(\frac{g\ N_2O-N}{g\ N}\right)=\frac{N_2O\ emissions\ \left(\frac{g\ N_2O-N}{h}\right)}{\left[TKN_{influent}-TN_{effluent}\right]\left(\frac{g\ N}{m^3}\right)\times wastewater\ (\frac{m^3}{h})}$$

Equation 8 – N_2O Emission factor.

In 2015, the estimated N_2O emission factor for Alcântara's WWTP was 0.1297 g N_2O-N.(g $N)^{-1}$ (12.9% of the in-coming nitrogen). This value was higher than 0.035% proposed by IPCC 2006, but it is considered to be in the range typically observed at WWTPs, by Kampschreur et al. 2009 and Foley et. al. 2010 (chapter 2.3).

To convert the emissions from kg N_2O-N to kg N_2O gas, a dimensionless conversion factor can be used (Equation 9).

$$N_2O\ emissions\ \left(\frac{kg\ N_2O}{h}\right)=\left(\frac{kg\ N_2O-N}{h}\right)\times\frac{44}{28}$$

Equation 9 – N_2O conversion factor [50].

Thus, using the N_2O conversion factor it is obtained 37.3 kg per hour of N_2O gas emitted from Alcântara's WWTP, in 2015.

To convert kg to m^3, mass densities of each gas compound are used, and those are obtained through Aspen Plus software program (Appendix II, Table 88). As such, estimated N_2O emissions are 20.7 m^3 per hour, which represented 0.29% of the total escaping air. The estimated steady state (Table 10) is taken into consideration and the estimated gas emission from the plant, during nitrification, is calculated (Table 11).

[16] TKN represents the sum of NH3-N plus organically bound nitrogen [49].

[17] TN represents the sum of NH3-N, NO3-N, NO2-N plus organically bound nitrogen [49].

Table 11 – Estimated Gas Emission, during denitrification, from Alcântara's WWTP, in 2015 (Appendix II, Table 88).

Escaping Air	kg/h	m^3/h	(m^3/m^3 Air) %	ppmv[18]
N2O	37.3	20.7	0.29%	2,947.5
N2	6,343.0	5,539.5	78.71%	-
CO2	379.8	211.1	3%	-
O2	1,657.0	1,266.9	18%	-
Total	**8,417.2**	**7,038.3**	**100%**	**-**

3.3 Maximizing N_2O production, in Alcântara's WWTP

Improved efficiencies and energy savings at WWTPs as well as maximizing energy recovery can open 'the way to resources' to achieve energy independence for WWTPs [51]. Focusing on the new nitrogen removal (chapter 2.11), N_2O can be the main final product.

SNDPR lab-studies have been experimentally demonstrated to compromise the advantage of the N_2O accumulation. In the present study, in order to maximize N_2O production it is estimated an emission factor around 50% of the in-coming nitrogen, adapted from the first case situation presented in SNDPR systems (chapter 2.14), since nitrate is most often the dominant end product of nitrification in WWTPs, also not all nitrogen compounds are completely converted in full scale WWTPs and different microbial communities can be expected, beyond only DGAOs.

Thus, using Equation 8 it is estimated an average of 2,198 kg N_2O-N per day (92 kg N_2O-N per hour) and using Equation 9 it is obtained 143.9 kg per hour of N_2O gas maximized, emitted in Alcântara's WWTP. Once again, the estimated steady state (Table 10) is taken into consideration and the estimated gas emission from the plant is calculated (Table 12), with N_2O maximized during denitrification.

Table 12 – Estimated Gas Emission, with N_2O maximized during denitrification, from Alcântara's WWTP (Appendix II, Table 88).

Escaping Air	kg/h	m^3/h	(m^3/m^3 Air) %	ppmv
N2O	143.9	80	1.1%	11,366.8
N2	6,275.1	5,480.3	77.9%	-
CO2	379.8	211.1	3%	-
O2	1,657.0	1,266.9	18%	-
Total	**8,455.9**	**7,038.3**	**100%**	**-**

[18] Parts per million by volume

3.4 Three Case Scenarios of N_2O Purification, in Alcântara's WWTP

Based on the most common industrial process for N_2O gas purification (e.g. purification of N_2O as a by-product in the synthesis of adipic acid) and, also, on membrane gas separation industrial processes (Lawerence K. Wang et al.), the present study has the purpose to evaluate three different case scenarios for N_2O gas purification, in Alcântara's WWTP, from an economic point of view.

The first and second scenarios can only reach 24% of N_2O in the waste gas (Annex VI, Flowsheet section). However, Alcântara's WWTP compromises a biogas cleaning system (CO_2 removal), thus N_2O gas can be sent to the biogas pre-treatment, and the waste gas, already containing 68% of N_2O, can enter the biogas combustion. The last case scenario can reach 24% of N_2O in the waste gas, in a first step, and is followed by a second step which reaches 99.7% of N_2O highly pure, that can be sold as an additional revenue, for the WWTP (Annex VI, Flowsheet section).

The use of membranes and suction pumps take place in the first case scenario, which compromises a vacuum system (Annex VI, P&ID section). The second case scenario has a compression system up to 3 bar, which is followed by a cooling system and also membranes (Annex VI, P&ID section). The third and last case scenario has a compression system up to 44 bar, also followed by cooling systems and membranes, compromising continuous swing adsorption and a unit of liquefaction (Annex VI, P&ID section). A brief summary is presented in Table 13.

Table 13 – N_2O gas Purification, in Alcântara's WWTP.

Case	Scenario 1	Scenario 2	Scenario 3
N_2O Emission Factor	50%	50%	50%
N_2O Purification	24%	24%	99.7%
Pressure	Vacuum system	Up to 3 bar	Up to 44 bar
Purpose	Biogas Pre-treatment	Biogas pre-treatment	Additional Revenue
Final N_2O Purification	68%	68%	99.7%
Objective	**Biogas Combustion**	**Biogas Combustion**	**Selling N_2O**

The reason to have N_2O compressed up to 44 bar is mainly due to the product specifications of a gas distribution company (*Air Liquide*), located in Portugal. Actually, *Air Liquide* sells N_2O cylinders with 99,6% of purity and 35 kg of capacity. The cost depends on the volume requested by the customer and it can be considered a value between 12 – 15€ per kg, for cylinders with 35 kg of capacity. The price information is obtained via email and N_2O datasheet of *Air Liquide* is presented in Annex III.

The Flowsheet and P&ID (Piping and Instrumentation Diagram) sections of each case scenario are followed by the respective abbreviation and symbology list (Annex VI).

3.5 Mass and Energy Balances

Balances are necessary in any production process of the Chemical Industry. The mass balances allow to control and account for the consumption of raw materials and the production of the final product. The energy balances allow to control and account for the released and provided energy, in each equipment of the process.

The mass balances are based on the principle of mass conservation (*Lavoisier*'s Law), which states that for any system closed to all transfers of matter and energy, the mass of the system must remain constant over time, as system cannot change quantity if it is not added or removed (Equation 10).

$$Mass_{in} + Mass_{generated} = Mass_{out} + Mass_{consumed}$$

Equation 10 – The Law of Conservation of Mass.

The energy balances are based on the principle of energy conservation (*First Law of Thermodynamics*), which states that the total energy of an isolated system is constant. Energy can be transformed from one form to another, but cannot be created or destroyed (Equation 11).

$$Energy_{accumulated} = Energy_{in} - Energy_{out}$$

Equation 11 – The Law of Conservation of Energy.

The mass balances of each case scenario are presented with the respective P&ID, in the flowsheet section, as well as physical state, temperature and pressure conditions (Annex VI).

3.6 Dimensioning the Equipment

A detailed explanation of the P&ID section is now going to be presented within each equipment section.

3.6.1 Compressors

Fans, blowers and compressors are differentiated by the method used to move the air, and by the system pressure they must operate against. The specific ratio, which is the ratio of the discharge pressure over the suction pressure, is used for defining the fans, blowers and compressors (Table 14).

Table 14 – Differences between Fans, Blowers and Compressors [52].

Equipment	Specific Ratio
Fans	Up to 1.11
Blowers	1.11 to 1.20
Compressors	> 1.20

In this case study, compressors are used for scenarios 2 and 3. A synoptic chart showing the main compressor types is presented in Figure 29.

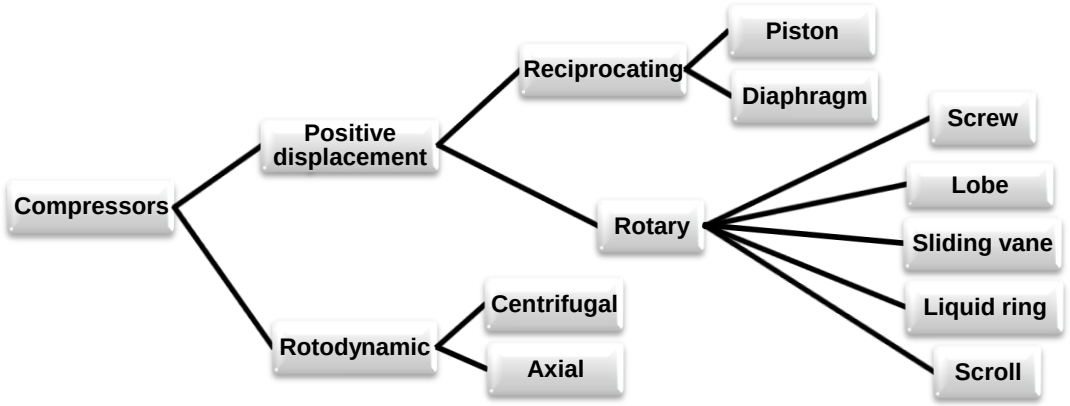

Figure 29 – Main Compressor Types [53].

Selection of the compressor type is based on the discharge pressure and inlet flow (Figure 30). The blue and red dashed lines represent scenarios 2 and 3, respectively.

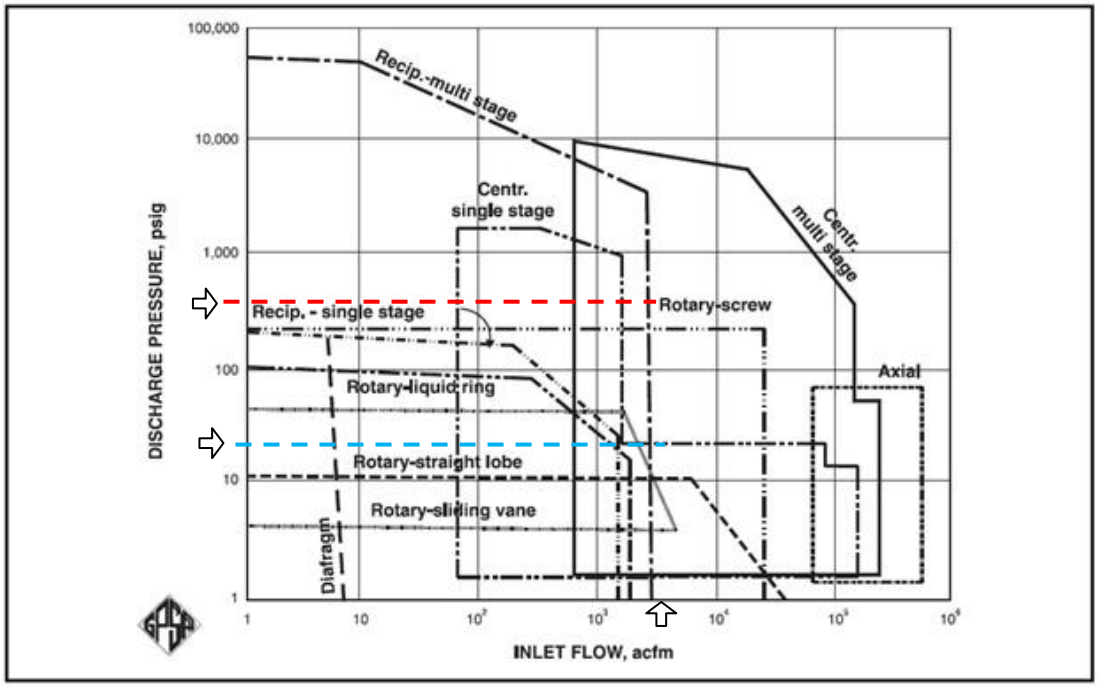

Figure 30 – Selection of the Compressor Type [54].

Discharge pressures and inlet flows are presented in Table 15.

Table 15 – Discharge Pressure and Inlet Flow of Scenarios 2 and 3.

Case	Scenario 2	Scenario 3
Discharge Pressure (bar)	3	44
Discharge Pressure (psig)	44	638
Inlet Flow (m^3/h)	7,038	7,038
Inlet Flow (cfm)	4,143	4,143
Compressor Type	**Centrifugal Single Stage**	**Centrifugal Multi Stage**

The compression ratio can be calculated using Equation 12, and it is limited by discharge temperature (Equation 13) since centrifugal compressors can only tolerate up to certain temperatures (Table 16).

$$Ratio_{stage} = \left(\frac{P_2}{P_1}\right)^{1/Number\ of\ Stages}$$

Equation 12 – Compression Ratio per Stage [55].

P_2: Discharge pressure, absolute

P_1: Inlet pressure, absolute

$$T_2 = T_1 \times (Ratio_{stage})^{\frac{n-1}{n}}$$

Equation 13 – Discharge Temperature [55].

T_2 : Stage discharge temperature (K)

T_1 : Stage inlet temperature (K)

n : Polytropic exponent

Table 16 – Centrifugal Compressors Limitations [56].

Centrifugal Compressors	Minimum Suction (Inlet)	Maximum Discharge (Outlet)
Pressure	Atmospheric or below	**100 bar**, for horizontally split compressors **1034 bar**, for radially split compressors
Temperature	Typically -19 to -46 ºC	Typically 204 to 232 ºC
Flow	As low as 100 $m^3\ h^{-1}$ As high as 680,000 $m^3\ h^{-1}$	-
Power	-	As low as 75 kW As high as 97 MW or more

For a specific gas, the limits to compression ratio are the mechanical and rotordynamic limitations on speed and also the number of stages that can be accommodated in a single body [56]. In a single stage system the air is compressed once, and in a dual stage the air is compressed twice [57].

An intercooler is any mechanical device used to cool a fluid between stages of a multi-stage heating process, typically a heat exchanger that removes waste heat in a gas compressor. Thus, discharge temperatures resulting from high compression ratios can usually be controlled by intercooling, so that the outlet temperature does not become too high [56].

In scenario 3, to compress the gas up to 44 bar, one stage only can't be used since the discharge temperature comes around 1,000ºC. Therefore, it is decided the use of two compressors, both with two stages, to take advantage of the heat generated by the compressors which is also generated by the compressor of scenario 2, with one stage only. Discharge pressure of the first compressor is up to 10 bar since the discharge temperature (nearly 230 ºC), comes around the maximum limit of the outlet temperatures reported by centrifugal compressors limitations (Table 16).

Table 17 shows the compression ratio per stage of each case scenario.

Table 17 – Compression Ratios of Scenarios 2 and 3.

Case	Scenario 2	Scenario 3	
Compressor	**C-101**	**C-101**	**C-102**
P_1 (bar)	1.01	1.01	10
P_2 (bar)	3	10	44
Nº of Stages	1	2	2
Compression Ratio	**2.96**	**3.14**	**2.10**

A polytropic process is often used to simplify and model complex processes. A common use is modelling compression and expansion processes when heat-transfer effects are presented [58]. An isentropic process can be described by Equation 14.

$$Pv^{\gamma} = constant$$

Equation 14 – Isentropic Process [58].

P: pressure

v: volume

γ: specific heat ratio

By replacing γ, by an arbitrary exponent n, it is defined a generalized process or polytropic process as presented in Equation 15.

$$Pv^{n} = constant$$

Equation 15 – Polytropic Process [58].

For certain values of n, Table 18 illustrates the special-case polytropic processes and Figure 31 shows these processes on P – v and T – s coordinates.

Table 18 – Special Cases of Polytropic Processes [58].

Process	Constant Property	Polytropic Exponent (n)
Isobaric	*P*	0
Isothermal	*T*	1
Isentropic	*s* or S	γ
Isochoric	*v* or V	$\pm\infty$

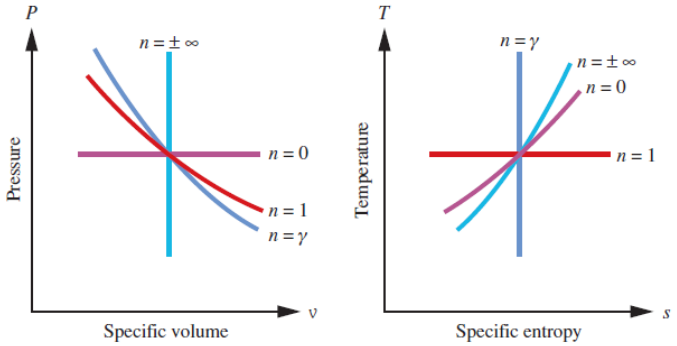

Figure 31 – P-v and T-s diagrams illustrating polytropic process paths for special cases of constant pressure (n = 0), constant temperature (n = 1), constante entropy (n = γ), and constant volume (n = $\pm\infty$) [58].

Figure 32 is useful for rough estimation of polytropic exponent, n. It connects the suction volume with the specific heat ratio, γ, which for air represents 1.406.

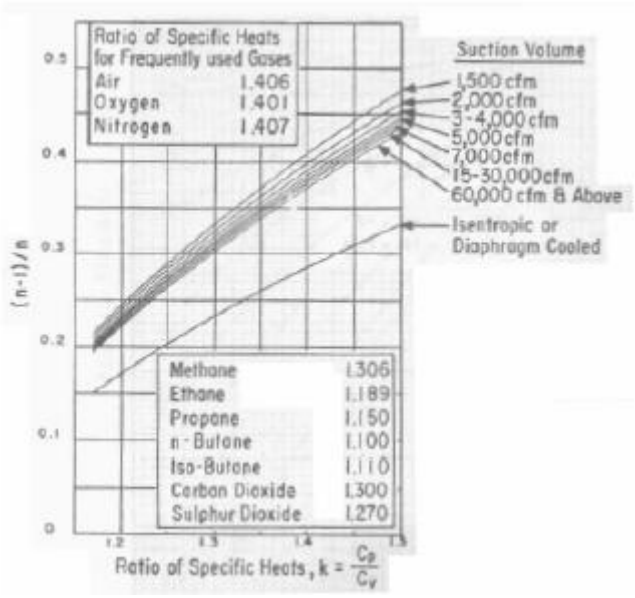

Figure 32 – Estimation of Polytropic Exponent, n [59].

Polytropic efficiency is usually used for centrifugal compressors (70% to 85%) [55] and it can be calculated using Equation 16.

$$n = \frac{\eta_p \gamma}{1 + \eta_p \gamma - \gamma} \leftrightarrow \eta_p = \frac{\left(\frac{\gamma - 1}{\gamma}\right)}{\left(\frac{n - 1}{n}\right)}$$

Equation 16 – Polytropic Efficiency [55].

n: Polytropic exponent

η_p: Polytropic efficiency (can also be provided by the compressor manufacturer)

γ: Ratio of specific heats

Thus, with polytropic exponent known, it is now possible to calculate the discharge temperatures of each compressor, using Equation 13. Table 19 shows the values used for calculation of discharge temperatures.

Table 19 – Discharge Temperatures of Scenarios 2 and 3.

Case	Scenario 2	Scenario 3	
Compressor	**C-101**	**C-101**	**C-102**
Suction volume (m^3/h)	7,038	7,038	720
Suction volume (cfm)	4,143	4,143	424
$\boldsymbol{\gamma}$ (air)	1.406	1.406	1.406
(n-1)/n	0.39	0.39	0.43
Polytropic exponent, $\boldsymbol{n}$	1.64	1.64	1.75
Polytropic efficiency, $\boldsymbol{\eta_p}$	74%	74%	67%
Inlet Temperature	25ºC / 298 K	25ºC / 298 K	28ºC / 301 K
Discharge Temperature	**182ºC / 455 K**	**193ºC / 466 K**	**141ºC / 414 K**

The inlet temperature of C-102 (28ºC) is associated to the heat transfer that occurs in the heat exchanger HE-101, which is calculated in the heat exchangers section (Table 22).

Table 20 shows the values used for calculation of suction and discharge volumes, for each compressor. This calculation is based on the Ideal Gas Law (Equation 17).

$$PV = n\,RT \leftrightarrow \rho = \frac{PM}{RT}$$

Equation 17 – Ideal Gas Law [55].

ρ : Mass density (kg/m^3)

P : Pressure (bar)

M : Molecular weight (kg/mol)

R : Gas constant (0.0000821 bar m^3 mol^{-1} K^{-1})

T : Temperature (K)

At 25ºC and 1.01 bar, the mass density of waste gas can be calculated, which is the ratio of the inlet mass flow rate (8,456 kg/h) over inlet volumetric flow rate (7,038 m^3/h). Thus, molecular weight of waste gas can be calculated, using Equation 17.

Table 20 – Suction and Discharge Volumes, of Scenarios 2 and 3.

Case	Scenario 2	Scenario 3	
Compressor	**C-101**	**C-101**	**C-102**
Inlet Temperature	25ºC / 298 K	25ºC / 298 K	28ºC / 301 K
Discharge Temperature	182ºC / 455 K	193ºC / 466 K	141ºC / 414 K
Inlet Pressure (bar)	1.01	1.01	10
Discharge Pressure (bar)	3	10	44
Molecular Weight (kg/mol)	0.029	0.029	0.029
Inlet Density, $\boldsymbol{\rho}$ (kg/m^3)	1.201	1.201	11.747
Discharge Density, $\boldsymbol{\rho}$ (kg/m^3)	2.329	7.587	37.587
Mass Flow Rate (kg/h)	8,456	8,456	8,456
Suction volume (m^3/h)	**7,038**	**7,038**	**720**
Discharge Volume (m^3/h)	**3,630**	**1,115**	**225**

At last, the polytropic head is calculated (Equation 18), then converting head to gas power (Equation 19), and accounting for mechanical losses in the compressor such as friction, gears, etc. (Equation 20), so total power is calculated (Equation 21).

$$W_p = \frac{P_1\, Z\, n}{\rho_1 (n-1)} \left[\left(\frac{P_2}{P_1} \right)^{\frac{n-1}{n}} - 1 \right]$$

Equation 18 – Polytropic Head [55].

W_p : Polytropic head (kN m kg^{-1})

P_1 : Stage inlet pressure (kPa)

P_2 : Stage discharge pressure (kPa)

n: Polytropic exponent

Z : average of inlet and discharge compressibility factors (Z~1)

$$Power_{gas} = \frac{W_p \times \sigma \times \rho}{3600 \times \eta_p}$$

Equation 19 – Power to Compress the Gas [55].

W_p : Polytropic head (kN m kg^{-1})

σ : Flow rate at inlet conditions (m^3/h)

ρ : Density at inlet conditions (kg/m^3)

η_p : Polytropic efficiency

$$Power_{losses} = Power_{gas}{}^{0,4}$$

Equation 20 – Power Losses [55].

$$Power_{total} = \frac{Power_{gas} + Power_{losses}}{\eta_{drive} \times \eta_{motor}}$$

Equation 21 – Total Power Required [55].

η_{drive} : Efficiency of the drive train, such as VFD[19] (95% assumed)

η_{motor} : Motor efficiency (95% assumed)

Table 21 shows the values used for calculation of total power required, for each compressor.

Table 21 – Suction and Discharge Volumes of Scenarios 2 and 3.

Case	Scenario 2	Scenario 3	
Compressor	**C-101**	**C-101**	**C-102**
Polytropic Head, $\boldsymbol{W_p}$ (kN m kg^{-1})	114	321	176
Polytropic exponent, $\boldsymbol{n}$	1.64	1.64	1.75
Inlet Pressure	1.01 bar / 101 kPa	1.01 bar / 101 kPa	10 bar / 1,000 kPa
Discharge Pressure	3 bar / 300 kPa	10 bar / 1,000 kPa	44 bar / 4,400 kPa
Inlet Flow Rate (m^3/h)	7,038	7,038	720
Inlet Density, $\boldsymbol{\rho}$ (kg/m^3)	1.201	1.201	11.747
Polytropic efficiency, $\boldsymbol{\eta_p}$	74%	74%	67%
$\boldsymbol{Power_{gas}}$ (kW)	362	989	617
$\boldsymbol{Power_{losses}}$ (kW)	10.6	15.7	13.1
$\boldsymbol{Power_{total}}$ **(kW)**	**412**	**1,114**	**698**

3.6.2 Heat Exchangers

Heat exchangers are critical elements in every process plant. While the majority of exchangers are the shell-and-tube type, there are several additional types namely finned tube, bare tube, plate-and-frame, spiral and plate coil [55].

In each case scenario (2 and 3), using heat exchangers has the purpose to cool the air which has been previously heated by the compressors. As such, heat that has been generated can be recovered and it can be useful, for example, to heat the final sludge of anaerobic digesters at Alcântara's WWTP.

[19] **Variable frequency drive:** frequency of the power that feeds the pump's motor.

- **Assumptions**

Steady operating conditions exist. The heat exchanger is well insulated so that heat loss to the surroundings is negligible and thus heat transfer from the hot fluid is equal to heat transfer to the cold fluid. Changes in the kinetic and potential energies of fluid streams are negligible. Heat transfer coefficients and fouling factors are constant and uniform. The thermal resistance of the inner tube is negligible since the tube is thin-walled and highly conductive [60].

Pre-treated wastewater is used as the cold stream (cold fluid) and waste gas is used as the hot stream (hot fluid).

- **Maximum Heat Transfer Rate**

In each case scenario (2 and 3), the cold fluid enters a counter-flow heat exchanger at 22ºC and 1.01 bar.

The heat capacity rates of the hot and cold fluids can be calculated using Equations 22 and 23, respectively.

$$C_{hot} = \dot{m}_{hot} \times C_{p,hot}$$

Equation 22 – Heat Capacity of the Hot Fluid [60].

$$C_{cold} = \dot{m}_{cold} \times C_{p,cold}$$

Equation 23 – Heat Capacity of the Cold Fluid [60].

C: heat capacity rate of the fluid (kW/ºC)
$\dot{m}$*:* flow rate of the fluid (kg/s)
C_p*:* specific heat of the fluid (kJ/kg ºC)

Then, the smaller of the two heat capacity rates, previously calculated, is selected (Equation 24).

$$C_{min} = C_{hot} \; or \; C_{cold}$$

Equation 24 – Smaller Heat Capacity Rate [60].

C_{min}*:* smaller heat capacity rate (kW/ºC)

The maximum temperature difference in the heat exchanger can be calculated using Equation 25.

$$\Delta T_{max} = T_{hot,in} - T_{cold,in}$$

Equation 25 – Maximum Temperature Difference [60].

ΔT_{max}*:* maximum temperature difference (ºC)
$T_{hot,in}$*:* inlet temperature of the hot fluid (ºC)
$T_{cold,in}$*:* inlet temperature of the cold fluid (ºC)

Therefore, the hot fluid cannot be cooled by more than ΔT_{max} and the cold fluid cannot be heated by more than ΔT_{max}.

Finally, the maximum heat transfer rate is determined (Equation 26).

$$\dot{Q}_{max} = C_{min} \times \Delta T_{max}$$

Equation 26 – Maximum Heat Transfer Rate [60].

$\dot{Q}_{max}$*:* maximum heat transfer rate (kW)

- **Outlet Temperatures of the Cold and Hot Streams**

The outlet temperatures of the cold and the hot streams are determined using Equations 27 and 28, respectively.

$$\dot{Q} = C_{cold}\left(T_{cold,out} - T_{cold,in}\right) \rightarrow T_{cold,out} = T_{cold,in} + \frac{\dot{Q}}{C_{cold}}$$

Equation 27 – Outlet Temperature of the Cold Stream [60].

$$\dot{Q} = C_{hot}\left(T_{hot,in} - T_{hot,out}\right) \rightarrow T_{hot,out} = T_{hot,in} - \frac{\dot{Q}}{C_{hot}}$$

Equation 28 – Outlet Temperature of the Hot Stream [60].

$\dot{Q}$*:* heat transfer rate (kW)

Table 22 shows the values used for calculation of outlet temperatures, of the cold and hot streams, as well as heat transfer rates that have been considered, for each heat exchanger.

Table 22 – Outlet Temperatures of the Cold and Hot Streams, of Scenarios 2 and 3.

Case	Scenario 2	Scenario 3	
Heat Exchanger	**HE-101**	**HE-101**	**HE-102**
$\boldsymbol{Flow\ Rate}_{\boldsymbol{hot}}$ (kg/h)	8,456	8,456	8,456
$\boldsymbol{Flow\ Rate}_{\boldsymbol{cold}}$ (m^3/h)	5.0	5.2	3.6
$\boldsymbol{Flow\ Rate}_{\boldsymbol{cold}}$ (kg/h)	4,979	5,178	3,585
$\dot{\boldsymbol{m}}_{\boldsymbol{hot}}$ (kg/s)	2.35	2.35	2.35
$\boldsymbol{C}_{\boldsymbol{p,hot}}$ (kJ/kg ºC)	1.03	1.03	1.02
$\boldsymbol{C}_{\boldsymbol{hot}}$ (kW/ºC)	**2.42**	**2.43**	**2.40**
$\dot{\boldsymbol{m}}_{\boldsymbol{cold}}$ (kg/s)	1.38	1.44	1.00
$\boldsymbol{C}_{\boldsymbol{p,cold}}$ (kJ/kg ºC)	3.81	3.81	3.81
$\boldsymbol{C}_{\boldsymbol{cold}}$ (kW/ºC)	5.27	5.48	3.79
$\boldsymbol{C}_{\boldsymbol{min}}$ (kW/ºC)	**2.42**	**2.43**	**2.40**
$\boldsymbol{T}_{\boldsymbol{hot,in}}$ (ºC)	182	193	141
$\boldsymbol{T}_{\boldsymbol{cold,in}}$ (ºC)	22	22	22
$\Delta\boldsymbol{T}_{\boldsymbol{max}}$ (ºC)	160	171	119
$\dot{\boldsymbol{Q}}_{\boldsymbol{max}}$ (kW)	387.6	414.04	285.3
$\dot{\boldsymbol{Q}}$ **(kW)**	**380**	**400**	**278**
$\boldsymbol{T}_{\boldsymbol{hot,out}}$ (ºC)	25	28	25
$\boldsymbol{T}_{\boldsymbol{cold,out}}$ (ºC)	94	95	95

In Table 22, flow rate of the cold fluid is assumed since it can manipulate the outlet temperature of this fluid, which should be not more than 100ºC once it is the boiling point of water. Also, it is considered a heat transfer rate ($\dot{Q}$) below the maximum heat transfer rate ($\dot{Q}_{max}$) since it can manipulate the outlet temperature of the hot fluid.

To convert the flow rate of the cold fluid it is used the mass density of water, which is obtained with Aspen Plus software program (Appendix II, Table 88). As well, the specific heats of each gas compound are obtained (Appendix II, Table 89). To calculate the specific heat of total waste gas it is taken into account the quantity (v/v %) that each gas compound represents in the total air.

- **Dimensioning**

Heat transfer area, of each heat exchanger, can now be calculated using Equation 29.

$$A = \frac{\dot{Q}}{U \times \Delta T_{mean}}$$

Equation 29 – Heat Transfer Area [55].

A: heat transfer area (m^2)

$\dot{Q}$: heat transferred (W)

U: overall heat transfer coefficient (W/m^2 ºC)

ΔT_{mean}: log-mean temperature difference between hot and cold streams (ºC)

Where:

$$\Delta T_{mean}\ (countercurrent) = F\frac{(T_{in} - t_{out}) - (T_{out} - t_{in})}{ln\frac{(T_{in} - t_{out})}{(T_{out} - t_{in})}}$$

Equation 30 – Log-mean Temperature Difference [55].

F: correction factor (F=1, for a true countercurrent exchanger)

T: inlet (T_{in}) and outlet (T_{out}) temperatures of the hot stream (ºC)

t: inlet (t_{in}) and outlet (t_{out}) temperatures of the cold stream (ºC)

Table 23 shows the values used for calculation of heat transfer areas.

Table 23 – Heat Transfer Areas, of Scenarios 2 and 3.

Case	Scenario 2	Scenario 3	
Heat Exchanger	**HE-101**	**HE-101**	**HE-102**
$\boldsymbol{T_{in}}$ (ºC)	182	193	141
$\boldsymbol{T_{out}}$ (ºC)	25	28	25
$\boldsymbol{t_{in}}$ (ºC)	22	22	22
$\boldsymbol{t_{out}}$ (ºC)	94	95	95
$\Delta\boldsymbol{T_{mean}}$ (ºC)	25.4	32.5	15.6
$\dot{\boldsymbol{Q}}$ (W)	380,000	400,000	278,000
$\boldsymbol{U}$ (W/m^2 ºC)	250	250	250
$\boldsymbol{A}$ (m^2)	**59.7**	**49.2**	**71.2**

For each heat exchanger it is used an approximate overall heat transfer coefficient (U) (Annex IV, Figure 55).

- **Tubes**

Standard diameters and wall thickness for steel tubes are given in Table 24.

Table 24 – Standard Dimensions for Steel Tubes [61].

Outside diameter (mm)	Wall thickness (mm)				
16	1.2	1.6	2.0	-	-
20	-	1.6	2.0	2.6	-
25	-	1.6	2.0	2.6	3.2
30	-	1.6	2.0	2.6	3.2
38	-	-	2.0	2.6	3.2
50	-	-	2.0	2.6	3.2

The tube thickness is selected to withstand the internal pressure and give and adequate corrosion allowance. The smaller diameters are preferred for most duties, as they will give more compact, and therefore cheaper, exchangers. Larger tubes would be selected for heavily fouling fluids [61].

Inside diameter of tubes can be calculated using Equation 31.

$$d_i = d_o - 2w$$

Equation 31 – Inside Diameter of Tubes [62].

d_i *:* inside diameter of tubes (m)
d_o *:* outside diameter of tubes (m)
w*:* wall thickness of tubes (m)

The preferred lengths of tubes are 6 ft. (1.83 m), 8 ft. (2.44 m), 12 ft. (3.66 m), 16 ft. (4.88 m), 20 ft. (6.10 m) and 24 ft. (7.32 m). For a given surface area, the use of longer tubes will reduce the shell diameter, which will generally result in a lower cost exchanger, particularly for high shell pressures [61].

Thus, the number of tubes in the shell, of each exchanger, can be calculated using Equation 32.

$$n_{tubes} = \frac{A}{A_s} = \frac{A}{\pi\, d_o\, L}$$

Equation 32 – Number of Tubes in the Shell [63].

A*:* heat transfer area (m^2)
A_s*:* surface area per tube (m^2)
d_o *:* outside diameter of tubes (m)
L*:* tube length (m)
n_{tubes} *:* number of tubes in the shell

Table 25 shows the values used for calculation of number of tubes.

Table 25 – Number of Tubes in the Shell, of Scenarios 2 and 3.

Case	Scenario 2	Scenario 3	
Heat Exchanger	**HE-101**	**HE-101**	**HE-102**
d_o (m)	0.025	0.025	0.025
d_i (m)	0.0186	0.0186	0.0186
w (m)	0.0032	0.0032	0.0032
π[20]	3.14	3.14	3.14
L (m)	7.32	7.32	7.32
A_s (m^2)	0.575	0.575	0.575
A (m^2)	59.7	49.2	71.2
n_{tubes}	**104**	**86**	**124**

- **Shell Diameter**

The following equations have the purpose to obtain the shell diameter, of each exchanger. Triangular pitch (P_t) is selected for each shell configuration. For triangular pitch, the area of the triangle, with vertices at the center of three tubes, is one-half of the area required to accommodate one tube (Figure 33).

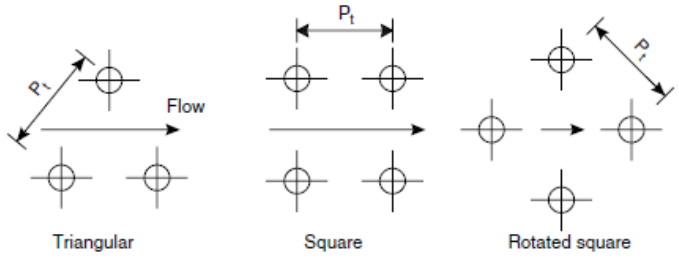

Figure 33 – Possible Shell Configurations, for exchangers [61].

Thus, the cross-sectional area per tube can be calculated using Equation 33.

$$A_{tube,\ triangular} = 2\ (PR\ d_o)^2\ \frac{\sqrt{3}}{4}$$

Equation 33 – Cross-sectional Area per tube [55].

$A_{tube,\ triangular}$ *:* cross-sectional area occupied by each tube, for triangular pitch (m^2)

PR*:* tube pitch ratio (usually 1.25, 1.285, 1.33 or 1.5)

d_o *:* outside diameter of tubes (m)

[20] The number **π** is a mathematical constant, the ratio of a circle's circumference to its diameter, commonly approximated as 3.14159.

The tight diameter can be calculated using Equation 34.

$$D_{tight} = 2\left(\frac{n_{tubes}\, A_{tube,\ triangular}}{\pi}\right)^{0,5}$$

Equation 34 – Tight Diameter [55].

D_{tight}: diameter of a circle that equates to the area for all tubes in the shell (m)
n_{tubes} : number of tubes in the shell

The cross-sectional corrected area can be calculated using Equation 35.

$$A_{corrected} = D_{tight}\, d_o \left(n_p - 1\right) + \left(n_{tubes}\ A_{tube,\ triangular}\right)$$

Equation 35 – Cross-sectional Corrected Area [55].

$A_{corrected}$: cross-sectional corrected area, to account for the pass partition (m^2)
d_o : outside diameter of tubes (m)
n_p : number of tube passes in the shell (usually 1-pass up to about 14)

Finally, minimum shell diameter can be calculated using Equation 36.

$$D_{s,\ min} = 2\left(\frac{A_{corrected}}{\pi}\right)^{0,5} + 2d_o$$

Equation 36 – Minimum Shell Diameter [55].

$D_{s,\ min}$: Minimum shell diameter (m)
$A_{corrected}$: cross-sectional corrected area (m^2)
d_o : outside diameter of tubes (m)

Table 26 shows the values used for calculation of minimum shell diameter.

Table 26 – Minimum Shell Diameter, of Scenarios 2 and 3.

Case	Scenario 2	Scenario 3	
Heat Exchanger	**HE-101**	**HE-101**	**HE-102**
$\boldsymbol{d_o}$ (m)	0.025	0.025	0.025
$\boldsymbol{PR}$	1.25	1.25	1.25
$\boldsymbol{A_{tube,triangular}}$ (m^2)	0.000846	0.000846	0.000846
$\boldsymbol{\pi}$	3.14	3.14	3.14
$\boldsymbol{n_{tubes}}$	104	86	124
$\boldsymbol{D_{tight}}$ (m)	0.334	0.304	0.365
$\boldsymbol{n_p}$	1	1	1
$\boldsymbol{A_{corrected}}$ (m^2)	0.088	0.072	0.105
$\boldsymbol{D_{s,\ min}}$ (m)	**0.384**	**0.354**	**0.415**

- **Shell Baffles**

The following Equations have the purpose to obtain the minimum number of baffles, of each exchanger. Minimum baffle spacing is generally one-fifth of the shell diameter and not less than 50.8 mm (Equation 37) [64].

$$L_{b,\ min} = \frac{1}{5} \times D_s$$

Equation 37 – Minimum baffle spacing [64].

$L_{b,\ min}$: Minimum baffle spacing (m)

D_s : Shell diameter (m)

Thus, minimum number of baffles can now be calculated, using Equation 38.

$$N_{b,\ min} = \frac{L}{L_{b,\ min}} - 1$$

Equation 38 – Minimum number of baffles [61].

L: tube length (m)

$L_{b,\ min}$: Minimum baffle spacing (m)

$N_{b,\ min}$: Minimum number of baffles

The baffle cuts vary from 20% to 49% with the most common being 20%-25%, and the optimum baffle cut is generally 20%, as it affords the highest heat transfer for a given pressure drop. Baffle cuts smaller than 20% can result in high pressure drop. As the baffle cut increases beyond 20%, the flow pattern deviates more and more from crossflow and can result in stagnant regions or areas with lower flow velocities; both of these reduce the thermal effectiveness of the bundle [65].

Table 27 shows the values used for calculation of number of baffles.

Table 27 – Minimum Number of Baffles, of Scenarios 2 and 3.

Case	Scenario 2	Scenario 3	
Heat Exchanger	**HE-101**	**HE-101**	**HE-102**
$D_{s,}$ (m)	0.384	0.354	0.415
$L_{b,min}$ (m)	0.077	0.071	0.083
L (m)	7.32	7.32	7.32
Baffle cut	20%	20%	20%
$N_{b,min}$	**94**	**103**	**87**

3.6.3 Drums

The Drums connected to the heat exchangers have the purpose to retain possible moisture content (H_2O) that may eventually come along with the waste gas. Waste gas reaches elevated temperatures when heated by compressors, so that water is in the gas phase. However, water may condensate when cooled by the exchangers (Figure 34).

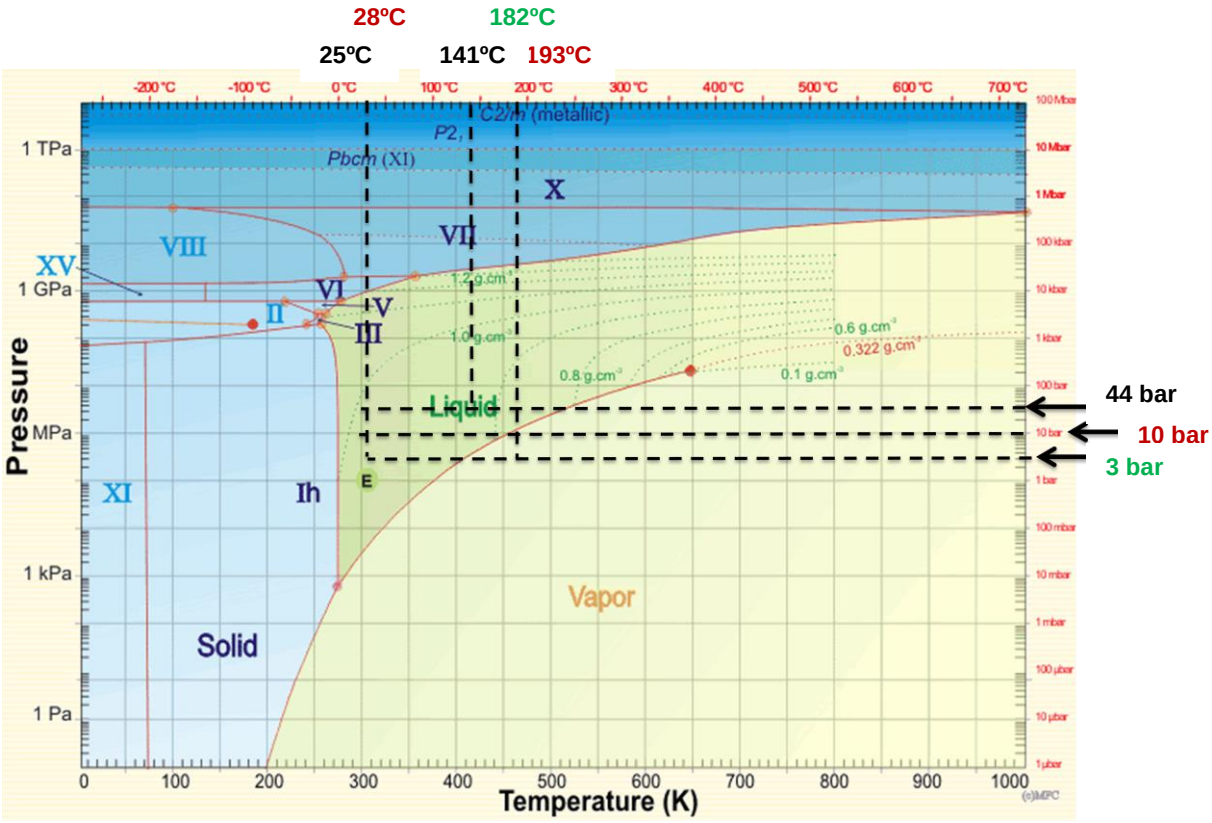

Figure 34 – Water Phases Diagram [66].

Table 28 shows the volumes assumed for drums.

Table 28 – Drum Volumes, of Scenarios 2 and 3.

Case	Scenario 2	Scenario 3
Drums	**D-101**	**D-101**
$\boldsymbol{V}$ (m^3)	**5**	**5**

3.6.4 Hydraulic Pumps

Power is required to pump the pre-treated wastewater across the exchanger's shell. Centrifugal pumps consume energy to develop the discharge pressure and to deliver flow. Therefore hydraulic power of the pump depends on these two parameters (Equation 39).

$$HP_{pump} = \frac{\Delta P_{total} \times \sigma}{\eta}$$

Equation 39 – Pump Hydraulic Power [67].

HP_{pump} : Pump hydraulic power (W)

ΔP_{total} : Total drop pressure (Pa)

σ : Pump flow rate (m^3/s)

η : Pump efficiency (90% assumed)

Usually each process stream is typically associated with a pair of pumps, so that replacement occurs in case one fails.

- **Pipelines**

Total drop pressure of each pipeline associated to the pumps can be calculated using Equation 40.

$$\Delta P_{total} = \Delta P_{line} + \Delta P_{tube\_accessories} + \Delta P_{height} + \Delta P_{control\_valves}$$

Equation 40 – Total Drop Pressure [68].

Where control valves represent 30% of the total drop pressure:

$$\Delta P_{total} = \frac{(\Delta P_{line} \times L_{tube}) + \Delta P_{tube\_accessories} + \Delta P_{height}}{0{,}7}$$

Equation 41 – Total Drop Pressure [68].

ΔP_{line} : Pipeline drop pressure (bar/m)

L_{tube} : Tube length (20-50m, for short pipelines)

$\Delta P_{acc.}$: Accessories such as valves (20-30% of ΔP_{line}, for short pipelines)

ΔP_{height} : A drop pressure of 1 bar corresponds to the water an unevenness of 10 m

Pipeline drop pressure can be determined from *Abaques de Paul Lefévre* handbook, which relates the inlet speed, viscosity and flow rate of a liquid. Putting it together, it's possible to get a unique point which defines the pipeline drop pressure. Also, the pipeline diameter can be known once it is associated with all these parameters (Figure 35) [69].

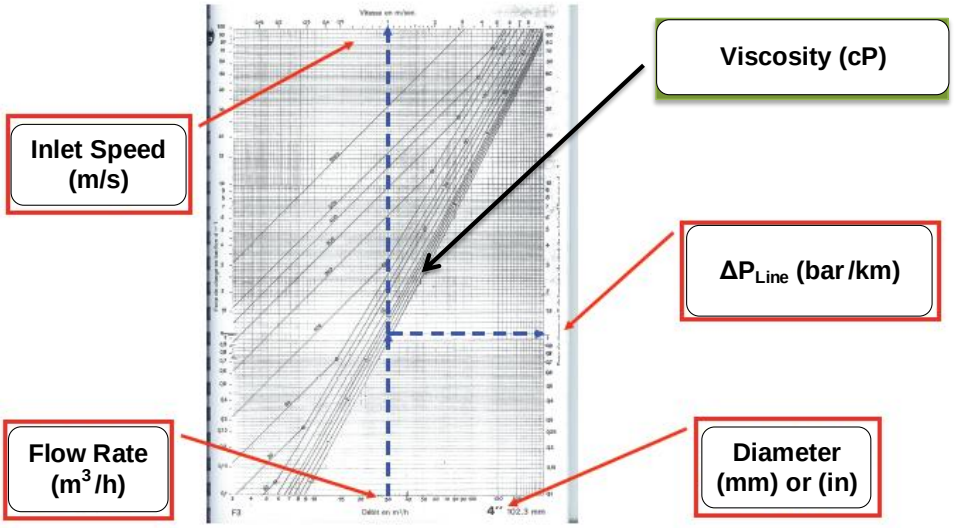

Figure 35 – Pipeline Drop Pressure (*Abaques de Paul Lefévre*).

It should be noted that the inlet speed must not exceed 1.5 m/s. Outlet speeds usually be in the range of 1 – 3 m/s [68]. The shell diameter is used to calculate the height drop pressure.

Table 29 shows the values used for calculation of pump hydraulic power.

Table 29 – Pump Hydraulic Power, of Scenarios 2 and 3.

Case	Scenario 2		Scenario 3		
Pumps	**P-101 A/B**	**P-102 A/B**	**P-101 A/B**	**P-102 A/B**	**P-103 A/B**
$\boldsymbol{\sigma}$ (m^3/h)	5	5	5.2	3.6	5
$\boldsymbol{\sigma}$ (m^3/s)	0.0014	0.0014	0.0014	0.001	0.0014
$\boldsymbol{Inlet\ Speed, v}$ (m/s)	0.29	0.29	0.3	0.46	0.29
Water Viscosity (at 21ºC, 1 atm)	1 cP	1 cP	1 cP	1 cP	1 cP
$\boldsymbol{Diameter, D}$ (m)	78 mm / 3in	78 mm / 3in	78 mm / 3in	53 mm / 2in	78 mm / 3in
$\boldsymbol{\Delta P_{line}}$ (bar/km)	0.15	0.15	0.15	0.52	0.15
$\boldsymbol{L_{tube}}$ (m)	40	40	40	40	40
$\boldsymbol{\Delta P_{acc.}}$ (bar) **30%**	0.0018	0.0018	0.0018	0.00624	0.0018
$\boldsymbol{D_{shell}}$ (m)	0.38	-	0.35	0.42	-
$\boldsymbol{\Delta P_{height}}$ (bar)	0.038	0	0.035	0.042	0
$\boldsymbol{\Delta P_{total}}$ **(bar)**	**0.066**	**0.011**	**0.062**	**0.098**	**0.011**
$\boldsymbol{\Delta P_{total}}$ (Pa)	6600	1100	6200	9800	1100
$\boldsymbol{\eta}$	90%	90%	90%	90%	90%
Power of 1 pump: $\boldsymbol{HP_{pump}}$ (W)	**10.2**	**1.7**	**9.9**	**10.9**	**1.7**
$\boldsymbol{\Delta P_{total} = P_2 - P_1 \rightarrow\rightarrow\ P_2 = \Delta P_{total} + P_1}$					
$\boldsymbol{P_1}$: pump inlet pressure (bar)	1	1	1	1	1
$\boldsymbol{P_2}$: pump outlet pressure (bar)	**1.07**	**1.01**	**1.06**	**1.10**	**1.01**

3.6.5 Membrane Modules

Figure 36 illustrates the process configuration for waste gas recovering with membranes, from U.S. EPA: Membrane separation system with vacuum pump **(A)** and membrane separation system with compressor **(B)** [70].

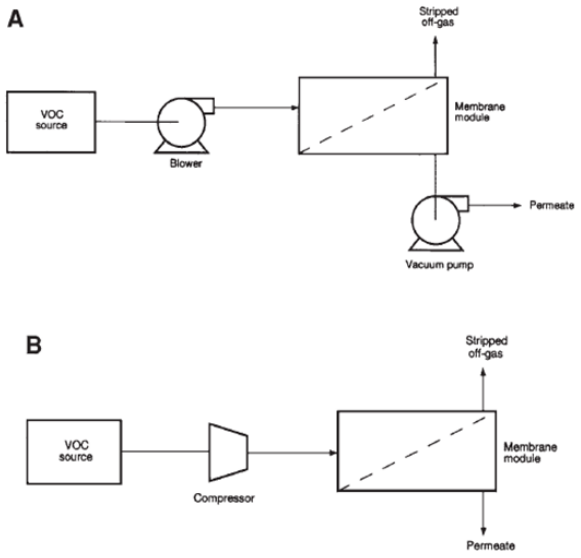

Figure 36 – Waste Gas Recovering with Membrane Modules, from U.S. EPA. (Lawerence K. Wang et al.)

Therefore, membranes are used in each case scenario (1, 2 and 3). Membrane gas separation is characterized by low material and energy consumption, operating at ambient temperature and also continuous operation [71].

The selection of membrane material is based on Figure 37, which involves the ideal selectivity (α) of polymeric membranes.

Membrane	$P \times 10^{14}$, mole m/(m^2 s PA)	α		
		N_2O–O_2	N_2O–N_2	O_2–N_2
Lestosil (present work)	98.6 ± 2.8	5.0 ± 0.2	10.1 ± 0.4	2.0 ± 0.01
Silicon rubber [11]	204	10.9	–	–
Cellulose acetate [11, 12]	592	6.3	30.4	2.7
Polydimethilsiloxane [12]	145.9	7.2	15.5	2.1
Perfluoro(2-methylen-4-methyl-1,3-dioxocy-clopenatne) [10]	7.0	0.5	2.2	4.2
Poly[bis(trifluoroethoxy)phosphazenene] [13]	72	6.1	14.6	2.4

Figure 37 – Permeability coefficient (P) and ideal selectivity (α) of polymeric membranes [71].

Once there is a great quantity of nitrogen gas (N_2) in the waste gas, it is selected cellulose acetate membranes for the present study.

Pure gas permeability coefficients for cellulose acetate membrane are presented in Table 30.

Table 30 – Pure Gas Permeability Coefficient (P), for Cellulose Acetate at 20ºC [72].

	P (m^3 m m^{-2} s^{-1} kPa^{-1})
CO_2	1.326 x 10^{-10}
N_2O	1.326 x 10^{-10}
O_2	0.21 x 10^{-10}

Thus, ideal selectivity of cellulose acetate can be calculated, and is presented in Table 31.

Table 31 – Ideal Selectivity (α), of Cellulose Acetate.

	α
P (N_2O/N_2)	30.4
P (N_2O/CO_2)	1
P (N_2O/O_2)	6.3

Since cellulose acetate membrane has the biggest permeability on N_2O and CO_2, it is assumed that only N_2 and O_2 will be separated from the waste gas. In each case scenario, two membranes are used for a better separation of the waste gas. As such, ideal selectivity is the parameter key that makes the mass balances change.

According to Ideal Gas Law, volumes are directly proportional to temperatures. Using Equation 17 (Ideal Gas Law) it can be calculated the inlet volumes of each membrane (Table 32). Temperature doesn't change in case scenario 1.

Table 32 – Inlet Membrane Volumes, of Scenarios 2 and 3.

Case	Scenario 2	Scenario 3
Membrane Modules	**MB-101**	**MB-101**
Inlet Temperature	25ºC / 298 K	25ºC / 298 K
Inlet Pressure (bar)	3	44
Molecular Weight (kg/mol)	0.029	0.029
Mass Flow Rate (kg/h)	8,456	8,456
Inlet Density, ρ (kg/m^3)	3.555	52.168
Inlet Volume (m^3/h)	**2,378**	**162**

Mass density, of each gas compound, is then maintained constant when entering the membranes (Table 33).

Table 33 – Inlet Membrane Conditions, of Scenarios 1, 2 and 3.

Case	Scenario 1	Scenario 2	Scenario 3
Stream	**S-103**	**S-105**	**S-107**
Temperature	25ºC / 298 K	25ºC / 298 K	25ºC / 298 K
Pressure (bar)	1.01	3	44
Waste gas Flow Rate (kg/h)	8,456	8,456	8,456
Waste gas Flow Rate (m^3/h)	7,038	2,378	162
Gas Compound	**Density, ρ (kg/m^3)**		
N_2O (g)	1.799	5.32	78.12
N_2 (g)	1.145	3.39	49.72
CO_2 (g)	1.798	5.32	78.11
O_2 (g)	1.307	3.87	56.79

- **Dimensioning**

Figure 38 shows an example of a vessel model, used for commercial and industrial membrane applications. Standard diameter and length, as well as, operational conditions are given in Table 34, for each membrane of each case scenario.

Figure 38 – Membrane Vessel [73].

Figure 39 shows an example of a roll membrane. Standard dimensions are also given in Table 34.

Figure 39 – Roll Membrane [74].

The required specifications of cellulose acetate are presented in Figure 40.

SPECIFICATIONS: WHITE PLAIN CELLULOSE ACETATE, CODE C

Pore Size (µm)	Bubble Point [1]		Flow Rate [2]		Porosity [3] (%)	Thickness [4] (µm)
	MPa	psi	Water (mL/min/cm²)	Air (L/min/cm²)		
0.20	≥0.25	≥37.1	16	2	66	125
0.45	≥0.17	≥25.9	35	4	68	125
0.80	≥0.068	≥10.0	160	14	72	125
3.00	≥0.034	≥5.0	500	54	78	135

- Wetting time: <3 seconds to wet a 47 mm diameter disk with aqueous 1% methylene blue
- Refractive index = 1.47
- Maximum Operating Temperature = 180°C
- Ash Content 1.5–3.5 µg/cm²

Definitions:
1. Bubble point is the minimum pressure required to force air through a membrane which has been prewet with water
2. Flow Rate indicates initial flow rate at 10 psi using a KGS 47 filter holder
   Water: using water prefiltered to 0.1 µm pore size
   Air: using prefiltered nitrogen at 10 psi
3. Porosity refers to the percent open area
4. Average thickness

Rolls, Plain White, 33 cm x 3 m

Pore Size (µm)	Roll
0.20	C020A330R
0.45	C045A330R
0.80	C080A330R

Figure 40 –Specifications of Cellulose Acetate [75].

Dimensions of membrane modules, in each case scenario, are presented in Table 34. In case scenario 1, having 4 lines is fundamental since there is a standard required total area for membrane vessels (0.341 m^2). The needed area of cellulose acetate must not exceed 0.341 m^2 since the permeate flow rate (J) is the critical variable to determinate the efficiency of the process. In case of scenario 1, using the initial flow rate (7,038 m^3/h) would result in 0.84 m^2 of needed area. Thus, 7,038 m^3/h flow rate is divided by 4.

Also, it is taken into consideration the bubble point, which is the minimum pressure required to force air through membrane, and the pore size which can manipulate flow rate entrances.

Table 34 –Membrane Modules Dimensions and Operational Conditions.

Case	**Scenario 1**		**Scenario 2**		**Scenario 3**	
Membrane Vessels	**MB – 101 A/B/C/D**	**MB – 102 A/B/C/D**	**MB - 101**	**MB - 102**	**MB - 101**	**MB - 102**
Model **[73]**	40E30N	40E30N	40E30N	40E30N	40E100	40E100
Elements	1	1	1	1	1	1
P_{max} (bar)	20	20	20	20	68	68
T_{max} (ºC)	49	49	49	49	49	49
Length	40 in / 1 m	40 in / 1 m	40 in / 1 m	40 in / 1 m	40 in / 1 m	40 in / 1 m
Diameter	4 in / 0.1 m	4 in / 0.1 m	4 in / 0.1 m	4 in / 0.1 m	4 in / 0.1 m	4 in / 0.1 m
Total Area (m^2)	0.341	0.341	0.341	0.341	0.341	0.341
Cellulose Acetate Membrane	**MB – 101 A/B/C/D**	**MB – 102 A/B/C/D**	**MB - 101**	**MB - 102**	**MB - 101**	**MB - 102**
Pore Size (µm)	0.8	0.8	0.8	0.2	0.2	0.2
Bubble Point (bar)	≥ 0.689	≥ 0.689	≥ 0.689	≥ 2.5	≥ 2.5	≥ 2.5
J, flow rate (L min^{-1} cm^{-2})	14	14	14	2	2	2
Porosity (%)	72	72	72	66	66	66
Thickness (µm)	125	125	125	125	125	125
Inlet Flow Rate (L min^{-1})	29,325	2,800	39,638	3,785	2,702	258
Area $_{Needed}$ (m^2)	0.209	0.02	0.283	0.189	0.135	0.013
Cellulose Acetate Roll	**MB – 101 A/B/C/D**	**MB – 102 A/B/C/D**	**MB - 101**	**MB - 102**	**MB - 101**	**MB - 102**
Width (cm)	33	33	33	33	33	33
Length (m)	3	3	3	3	3	3
Model	C080A330R	C080A330R	C080A330R	C020A330R	C020A330R	C020A330R

Expected membrane lifetime is around 3 to 5 years [76]. In the present study, it is considered 3 years of a membrane lifetime.

3.6.6 Vacuum Pumps

In case of scenario 1, vacuum pumps are used. The energy consumption is determined by the power consumption of the vacuum pump. The power requirement can be calculated using Equation 42.

$$P = \frac{n\,RT}{\eta} ln \frac{P_h}{P_l}$$

Equation 42 –Power Consumption of a Vacuum Pump [77].

η: pump efficiency (50% assumed)
n: number of moles to be pumped per second (mol/s)
R : Gas constant (8.31 J mol^{-1} K^{-1})
T : Temperature (K)
P_h: upstream pressure (inlet)
P_l: downstream pressure (outlet)

Table 35 shows the values used for the calculation of power consumptions. Molecular weight is calculated using Equation 17 (Ideal Gas Law). For the vacuum system it is assumed a drop pressure of 0.1 bar every time the waste gas goes through the pump.

Table 35 – Power Consumption of Vacuum Pumps, of Scenario 1.

Case	**Scenario 1**	
Streams	**S-106**	**S-108**
Vacuum Pumps	**VP-101 A/B/C/D**	**VP-102 A/B/C/D**
$\boldsymbol{T}$ (K)	298	298
$\boldsymbol{R}$ (J mol^{-1} K^{-1})	8.31	8.31
Inlet $\boldsymbol{P_h}$(bar)	1	0.9
Outlet $\boldsymbol{P_l}$(bar)	0.9	0.8
$\boldsymbol{\eta}$ (%)	50	50
Air density, $\boldsymbol{\rho}$ (kg/m^3)	1.48	1.74
Molecular weight (kg/mol)	0.036 (P=1bar)	0.047 (P=0.9bar)
Mass flow rate (kg/h)	248	143
Flow rate (mol/h)	6,867	3,024
Flow rate (mol/s)	1.91	0.84
Power of 1 vacuum pump: P (W)	**995.44**	**490.1**

3.6.7 Adsorption Columns

Pressure swing adsorption (PSA) is a technology used to separate some gas species from a mixture of gases under pressure according to the species molecular characteristics and affinity for an adsorbent material. It operates at near-ambient temperatures and specific adsorptive materials (e.g., zeolites, activated carbon, molecular sieves) are used as a trap, preferentially adsorbing the target gas species at high pressure. Regeneration step occurs when the process then swings to low pressure to desorb the adsorbed material.

Adsorbents for PSA systems are usually very porous materials because of their large specific surface area. Using two adsorbent vessels allows near-continuous production of the target gas (continuous swing adsorption).

- **CO_2 Capture By Adsorption**

Adsorption-desorption isotherms of activated carbon, zeolite-13X, and natural zeolites are presented in Figure 41. In the present study, CO_2 capture is made with activated carbon as the adsorbent material.

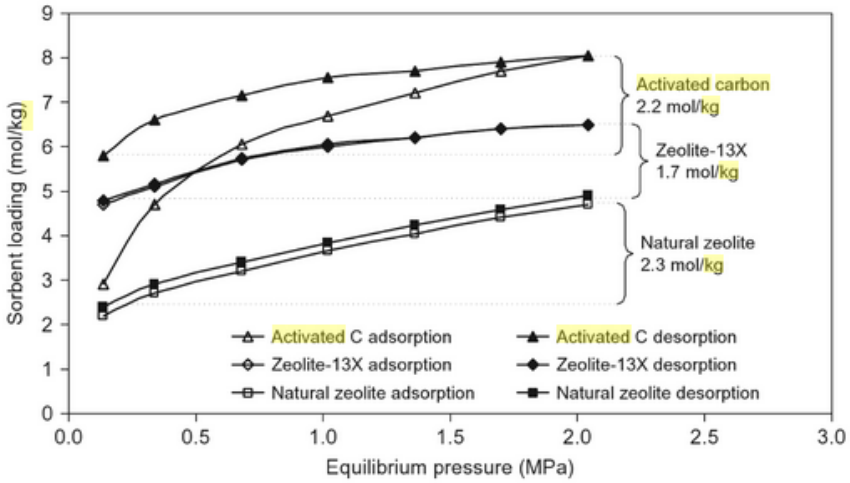

Figure 41 – Adsorption-desorption isotherms of adsorptive materials, at 25ºC [78].

Activated carbon (AC) has the highest CO_2 adsorption across most of the pressure range as well as the steepest adsorption isotherm, reaching 8 mol per kg at 2 MPa (20 bar). However, the desorption isotherm shows a high degree of hysteresis, reducing the working capacity over the pressure range shown to ~ 2.2 mole per kg. Zeolite-13x shows an intermediate adsorption capacity, with very low hysteresis. Natural zeolite has the lowest adsorption capacity, little more than half that of activated carbon at 2 MPa, but the steeper isotherm and relatively low hysteresis result in a working capacity over this pressure range of 2.3 mole per kg, marginally higher than activated carbon [78].

Once operational pressure, in the present study, is up to 44 bar then CO_2 adsorption isotherms of activated carbon can be found in Figure 42. In this figure other adsorptive materials are included, but they are not relevant for the present study.

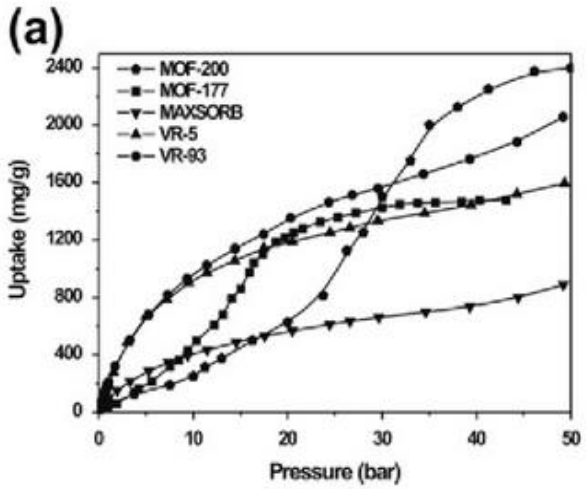

Figure 42 – CO_2 adsorption isotherms in a gravimetric (mg/g) basis on VR carbon molecular sieves samples, at 25ºC and up to 50 bar. MOF materials with exceptional adsorption properties and commercial activated carbon MAXSORB are included for the sake of comparison [79].

Carbonaceous adsorbents such as activated carbon (AC) have been widely used for CO_2 capture due to their wide availability, low cost, high thermal stability and low sensitivity to moisture. However, their application is limited to treat high pressure gases [80].

Table 36 shows considered values used for the desorption and adsorption processes, which are based on Figures 41 and 42, respectively.

Table 36 – Adsorption and Desorption Uptakes.

Case	Scenario 3
Adsorption Columns	**AC-201 A/B**
Adsorption Uptake (mg CO_2 / g AC)	790
Adsorption Pressure (bar)	44
Desorption Uptake (mol CO_2 / kg AC)	5.8
Desorption Pressure (bar)	2
Activated Carbon	Commercial

- **Regeneration Step**

Considering that the isosteric heat of adsorption of CO_2 on carbon materials is quite low (around 20 kJ/mol), the weak adsorbate-adsorbent interaction could anticipate an easy regeneration compared to other porous solids (e.g. zeolites). Silvestre-Albero et al. studied the behavior of carbon molecular sieve monoliths under repeated cycles from vacuum to high pressure (50 bar) at room temperatures (25ºC). As shown in Figure 43, CO_2 adsorption on carbon materials is completely reversible, with no loss of adsorption capacity over the whole pressure range [79].

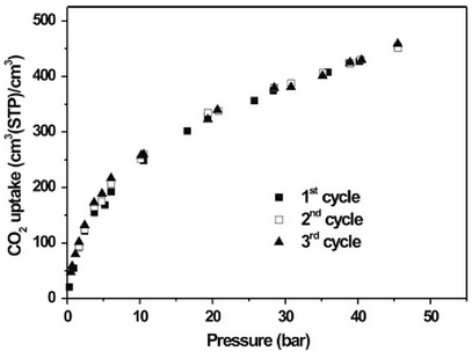

Figure 43 – CO_2 isotherms for activated carbon monolith VR-93 at 25ºC and up to 50 bar after different adsorption-desorption cycles, in a volumetric basis (cm^3/cm^3) [79].

A similar behavior in terms of regenerability was described in the literature for sawdust-based and N-doped porous carbons with no noticeable change in the kinetics of desorption and CO_2 uptake at atmospheric pressure and room temperature [79].

- **Activated Carbon (AC) and Regenerating Air**

Table 37 shows considered values used for the calculation of activated carbon quantity. CO_2 molecular weight is obtained with Aspen Plus software program (Appendix II, Table 87).

Table 37 – Activated Carbon.

Case	Scenario 3
Adsorption Columns	**AC-201 A/B**
CO_2 Molecular Weight (g mol^{-1})	44.01
Adsorption Uptake (kg CO_2 / kg AC)	**0.79**
CO_2 flow rate (kg h^{-1})	379.8
Activated Carbon $_{needed}$ (kg AC)	481
Desorption Uptake (kg CO_2 / kg AC)	**0.255**
Desorption Uptake (mol CO_2 / kg AC)	5.8
Activated Carbon $_{needed}$ (kg AC)	**1,488** ⇦

Total adsorption occurs in the presence of 481 kg of activated carbon, but total desorption requires 1.5 ton of activated carbon, due to adsorbate-adsorbent interaction. Therefore, it is considered that each adsorption column will have 1.5 ton of activated carbon. Swing operation takes place every time the column completes one hour of handling CO_2 adsorption/desorption.

In the desorption process, it is considered the use of a general regenerating air, with 21% O_2 and 79% N_2. It is assumed 500 kg/h of air flow rate (Table 38).

Table 38 – Regeneration Step.

Case	Scenario 3
Adsorption Columns	**AC-201 A/B**
Desorption Pressure (bar)	2
Air flow rate (kg h^{-1})	500
Air flow rate (m^3 h^{-1})	213
Temperature (ºC)	25
Air density, ρ (kg/m^3)	**2.34**

Mass densities of each gas compound (N_2 and O_2) at 2 bar are obtained using Aspen Plus software program (Appendix II, Table 88). To calculate air mass density it is taken into account the quantity (v/v %) that each gas compound represents in the total air.

The typical lifetime of granular activated carbon (GAC) is between 100 and 600 days. In the present study, 350 days are considered for GAC lifetime [81].

- **Dimensioning**

The bed density can be expressed as Equation 43.

$$\rho_{bed} = \rho_{GAC} * (1 - \varepsilon)$$

Equation 43 – Bed Density [81].

ρ_{bed} : bed density (kg/m^3)
ρ_{GAC} : granular activated carbon density (kg/m^3)
ε : bed porosity (usually 0.35-0.45)

Therefore, the GAC volume can be calculated using Equation 44.

$$V_{GAC} = \frac{m_{GAC}}{\rho_{bed}}$$

Equation 44 – GAC Volume [81].

V_{GAC} : granular activated carbon volume (m^3)
m_{GAC} : granular activated carbon weight (kg)

The volume of the adsorber, should account for bed expansion and maintenance, thus, the activated carbon occupies 66% of the total adsorber column, giving rise to Equation 45.

$$V_{ads} = 1.5 * V_{GAC}$$

Equation 45 – Adsorber Volume [82].

V_{ads} : adsorber column volume (m^3)

The relation between radius (r) and diameter (D) is given by Equation 46.

$$D = 2\,r \;\leftrightarrow r = \frac{D}{2}$$

Equation 46 – Adsorber Radius.

The relation between height (H) and diameter (D), for activated carbon columns design, is given by Equation 47.

$$\frac{H}{D} = 10 \leftrightarrow H = 10\,D$$

Equation 47 – Relation between Height and Diameter, for Adsorbers [83].

Thus, adsorber diameter can be calculated using Equation 48.

$$\rightarrow V_{ads} = \pi\, r^2 * H \;\leftrightarrow V_{ads} = \frac{\pi\, D^2}{4} * 10\, D = \frac{5\,\pi\, D^3}{2} \rightarrow D = \sqrt[3]{\frac{2\,V_{ads}}{5\,\pi}}$$

Equation 48 – Adsorber Diameter.

V_{ads} : adsorber column volume (m^3)
D : adsorber column diameter (m)

Table 39 shows considered parameters used for the fixed bed adsorbers.

Table 39 – Parameters of Adsorbers.

Case	Scenario 3
Adsorption Columns	**AC-201 A/B**
$\boldsymbol{\rho_{bed}}$ (kg/m^3)	300
$\boldsymbol{\rho_{GAC}}$ (kg/m^3)	500 **[84]**
$\boldsymbol{\varepsilon}$	0.4
$\boldsymbol{V_{GAC}}$ (m^3)	4.96
$\boldsymbol{m_{GAC}}$ (kg)	1,488
$\boldsymbol{V_{adsorber}}$ (m^3)	7.44
$\boldsymbol{D}$ (m)	0.982
$\boldsymbol{H/D}$ **ratio**	10
$\boldsymbol{H}$ (m)	9.82
$\boldsymbol{\pi}$	3.14

3.6.8 Buffer Tank

The purpose of using a buffer tank in case of scenario 3 is to make sure that it compensates the volume discharged by the adsorption column when swing operation occurs. In fact, when the adsorber gets empty (to be replaced by the regeneration step) then the buffer tank gets a little more filled of waste gas. Also, the buffer tank allows collecting a recycle that comes from the liquefaction unit.

Table 40 shows the assumed volume for buffer tank, which is the same volume used in each adsorption column.

Table 40 – Buffer Tank Volume.

Case	Scenario 3
Buffer Tank	**BF-201**
$\boldsymbol{V}$ (m^3)	**7.44**

3.6.9 Liquefaction Unit

Liquefaction is a term used to refer to any process which either generates a liquid from a solid or gas, or generates a non-liquid phase which behaves in accordance with fluid dynamics.

In case of scenario 3, the liquefaction unit has the purpose to partially liquefy the gas stream to obtain a gas mixture containing N_2O and non-condensation gas, and also to generate purified liquid N_2O, for storage and distribution. Part of the gas mixture which has been generated goes back again to the buffer tank, so that some N_2O can be recovered (recycling process). Table 41 shows the initial parameters of the waste gas, before entering the liquefaction unit.

Table 41 – Initial Mass Balances.

Case	Scenario 3	
Stream	**S-204**	
Mass Fraction	**(m/m)**	**(kg/h)**
N_2O (g)	74.9%	143.9
N_2 (g)	3.5%	6.8
CO_2 (g)	0%	0
O_2 (g)	21.6%	41.6
Total	**100%**	**192.3**
Temperature (ºC)	**25**	

Aspen Plus software program is used for this section. The second gas compound in a great quantity is O_2, thus in the present study it is considered a binary analysis (Figure 44).

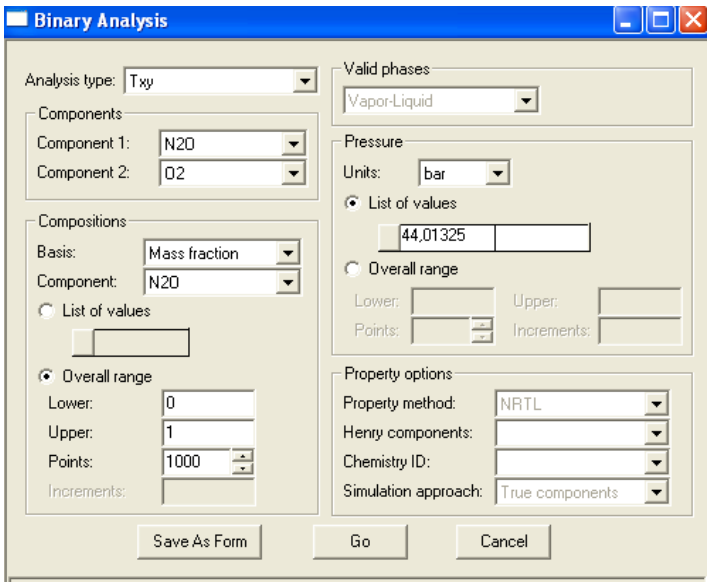

Figure 44 – Binary Analysis of Aspen Plus Software Program (1/5).

At 75%, N_2O begins to liquefy if the temperature is cooled below -1.42 ºC (Figure 45).

Binary analysis results

PRES	MASSFRAC N2O	TOTAL TEMP	TOTAL KVL N2O	TOTAL KVL O2	LIQUID GAMMA N2O	LIQUID GAMMA O2	VAPOR MASSFRAC N2O	VAPOR MASSFRAC O2	LIQUID MASSFRAC N2O	LIQUID MASSFRAC O2
bar		C								
44,01325	0,982983	-1,420417	0,7041072	13,42677	1	1	0,751811	0,248189	0,982983	0,017017
44,01325	0,983984	-0,5993295	0,7188355	13,55902	1	1	0,7650984	0,2349016	0,983984	0,016016
44,01325	0,984985	0,2267545	0,7338763	13,69257	1	1	0,778561	0,221439	0,984985	0,015015
44,01325	0,985986	1,057742	0,7492341	13,82742	1	1	0,792197	0,207803	0,985986	0,014014
44,01325	0,986987	1,893535	0,7649135	13,96355	1	1	0,8060049	0,1939951	0,986987	0,013013
44,01325	0,987988	2,734032	0,7809193	14,10096	1	1	0,8199828	0,1800172	0,987988	0,012012
44,01325	0,988989	3,579124	0,7972559	14,23962	1	1	0,8341284	0,1658716	0,988989	0,011011
44,01325	0,98999	4,4287	0,8139277	14,37954	1	1	0,8484395	0,1515605	0,98999	0,01001
44,01325	0,990991	5,282643	0,8309391	14,52068	1	1	0,8629136	0,1370864	0,990991	0,00900901
44,01325	0,991992	6,14083	0,8482943	14,66304	1	1	0,8775479	0,1224521	0,991992	0,00800801

Figure 45 – Binary Analysis of Aspen Plus Software Program (2/5).

It is intended to liquefy 99.9% of pure liquid N_2O and 0.1% remains for liquid impurities, such as O_2 and N_2. The number of points to reach 99.9% is 16 below 75% (Figure 46).

Binary analysis results

PRES	MASSFRAC N2O	TOTAL TEMP	TOTAL KVL N2O	TOTAL KVL O2	LIQUID GAMMA N2O	LIQUID GAMMA O2	VAPOR MASSFRAC N2O	VAPOR MASSFRAC O2	LIQUID MASSFRAC N2O	LIQUID MASSFRAC O2
bar		C								
44,01325	0,990991	5,282643	0,8309391	14,52068	1	1	0,8629136	0,1370864	0,990991	0,00900901
44,01325	0,991992	6,14083	0,8482943	14,66304	1	1	0,8775479	0,1224521	0,991992	0,00800801
44,01325	0,992993	7,003136	0,8659976	14,8066	1	1	0,8923395	0,1076605	0,992993	0,00700701
44,01325	0,993994	7,869428	0,884053	14,95133	1	1	0,9072854	0,0927146	0,993994	0,00600601
44,01325	0,994995	8,739572	0,9024644	15,09723	1	1	0,9223821	0,0776178	0,994995	0,00500501
44,01325	0,995996	9,613426	0,9212356	15,24426	1	1	0,9376263	0,0623737	0,995996	0,004004
44,01325	0,996997	10,49085	0,9403704	15,39241	1	1	0,9530141	0,0469859	0,996997	0,003003
44,01325	0,997998	11,37168	0,9598723	15,54165	1	1	0,9685417	0,0314582	0,997998	0,002002
44,01325	0,998999	12,25578	0,9797448	15,69196	1	1	0,9842051	0,0157948	0,998999	0,001001

Figure 46 – Binary Analysis of Aspen Plus Software Program (3/5).

Then, 16 points above 75% will give a gas mixture containing 56.4% of N_2O and 43.6% of non-condensation gas. Also, it is possible to know the temperature at which waste gas must be cooled, - 14ºC approximately (Figure 47).

Binary analysis results

PRES	MASSFRAC N2O	TOTAL TEMP	TOTAL KVL N2O	TOTAL KVL O2	LIQUID GAMMA N2O	LIQUID GAMMA O2	VAPOR MASSFRAC N2O	VAPOR MASSFRAC O2	LIQUID MASSFRAC N2O	LIQUID MASSFRAC O2
bar		C								
44,01325	0,966967	-13,82121	0,5069954	11,4923	1	1	0,5635837	0,4364163	0,966967	0,033033
44,01325	0,967968	-13,08881	0,5173834	11,60316	1	1	0,5740042	0,4259958	0,967968	0,032032
44,01325	0,968969	-12,35057	0,5280066	11,71535	1	1	0,5846013	0,4153987	0,968969	0,031031
44,01325	0,96997	-11,60649	0,5388695	11,82888	1	1	0,5953759	0,4046241	0,96997	0,03003
44,01325	0,970971	-10,85662	0,549977	11,94374	1	1	0,6063289	0,3936711	0,970971	0,029029
44,01325	0,971972	-10,10097	0,5613339	12,05994	1	1	0,6174611	0,3825389	0,971972	0,028028
44,01325	0,972973	-9,33958	0,572945	12,17749	1	1	0,628773	0,371227	0,972973	0,027027
44,01325	0,973974	-8,572491	0,5848151	12,29638	1	1	0,6402652	0,3597348	0,973974	0,026026
44,01325	0,974975	-7,799742	0,5969491	12,41661	1	1	0,651938	0,348062	0,974975	0,025025
44,01325	0,975976	-7,021379	0,6093519	12,53819	1	1	0,6637916	0,3362084	0,975976	0,024024

Figure 47 – Binary Analysis of Aspen Plus Software Program (4/5).

Figure 48 shows the vapor-liquid phases diagram from Aspen binary analysis, where T-y and T-x represent the vapor and liquid phases, respectively.

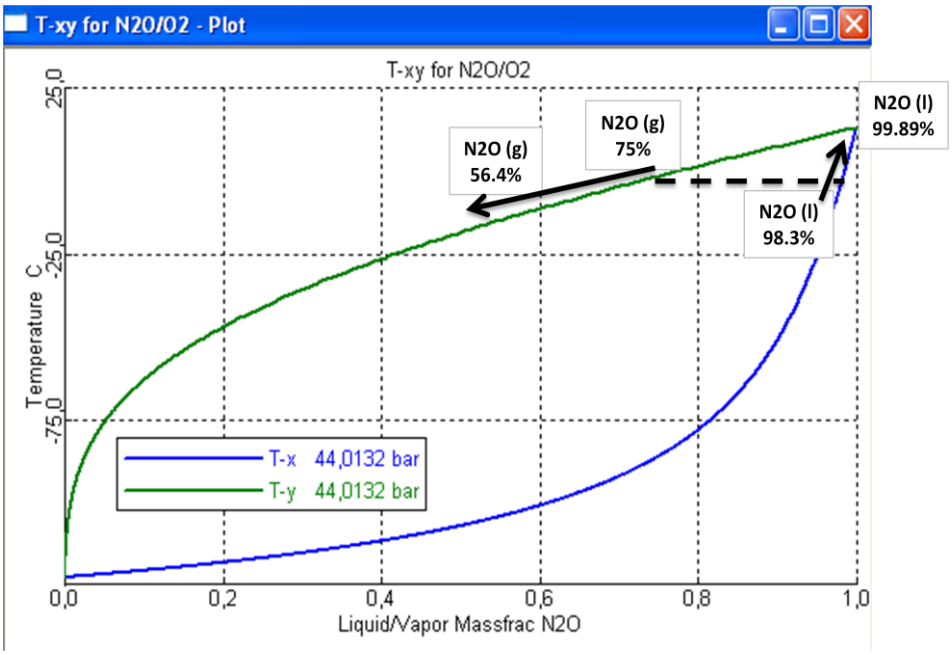

Figure 48 – Binary Analysis of Aspen Plus Software Program (5/5).

Thus, outlet quantities in the liquefaction unit can be calculated (Table 42). Gas stream 206 containing 56.4% of N_2O and 43.6% of non-condensation gas.

Table 42 – Mass Balances.

Case	Scenario 3			
Stream	**S-204**		**S-206**	
Mass Fraction	**(m/m)**	**(kg/h)**	**(m/m)**	**(kg/h)**
N_2O (g)	74.9%	143.9	56.4%	108.4
N_2 (g)	3.5%	6.8	6.1%	11.78
CO_2 (g)	0%	0	0%	0
O_2 (g)	21.6%	41.6	37.5%	72.13
Total	**100%**	**192.3**	**100%**	**192.3**
Temperature (ºC)	**25**		**-14**	

For the mass balance get closed, it is fundamental to have 42.5% of gas recycled, coming from stream 206 (Table 43).

Table 43 – Mass Balances (S-207 = 0.425*S-206; S-208 = S-206 – S-207).

Case	Scenario 3							
Stream	**S-204**		**S-206**		**S-207**		**S-208**	
Mass Fraction	**(m/m)**	**(kg/h)**	**(m/m)**	**(kg/h)**	**(m/m)**	**(kg/h)**	**(m/m)**	**(kg/h)**
N_2O (g)	74.9%	143.9	56.4%	108.36	56.4%	46.05	56.4%	62.31
N_2 (g)	3.5%	6.8	6.1%	11.784	6.1%	5.01	6.1%	6.78
CO_2 (g)	0%	0	0%	0	0%	0	0%	0
O_2 (g)	21.6%	41.6	37.5%	72.13	37.5%	30.65	37.5%	41.47
Total	**100%**	**192.3**	**100%**	**192.3**	**100%**	**81.72**	**100%**	**110.56**
Temperature (ºC)	**25**		**-14**		**-14**		**-14**	

Therefore, mass balances of streams 205 and 209 can be calculated (Table 44). For the calculation of S-205 outlet temperature, it is taken into account the total flow rates of streams 204, 207 and 205, and also the temperatures of streams 204 and 207.

Table 44 – Mass Balances (S-205 = S-207 + S-204; S-209 = S-205 – S-206).

Case	Scenario 3			
Stream	**S-205**		**S-209**	
Mass Fraction	**(m/m)**	**(kg/h)**	**(m/m)**	**(kg/h)**
N_2O (g)	69.3%	189.98	99.877%	81.62
N_2 (g)	4.3%	11.798	0.017%	0.014
CO_2 (g)	0%	0	0%	0
O_2 (g)	26.4%	72.22	0.106%	0.09
Total	**100%**	**273.99**	**100%**	**81.72**
Temperature (ºC)	**13.4**		**-14**	

To convert the mass balances to volumetric balances, mass densities of each gas compound are used and obtained with Aspen Plus software program (Appendix II, Table 88).

- **Maximum Heat Transfer Rate**

A liquefier is similar to a heat exchanger. However, outlet temperature of the hot stream is much lower in a liquefaction unit, comparing to outlet temperatures of heat exchangers, previously calculated. Thus, the following presented values are obtained using the same equations that have been previously used for dimensioning, in heat exchangers section.

In case of scenario 3, the liquefier has the purpose to cool the waste gas up to -14ºC. Ethylene glycol is used as the cold stream (cold fluid) and waste gas is used as the hot stream (hot fluid). The reason choosing ethylene glycol as refrigerant is mainly due to the fact that this glycol water (with 40% of ethylene glycol content) has a freezing point at -23.9ºC. Therefore, water doesn't freeze at negative temperatures [85].

Table 45 shows the calculated values, which have been considered for the liquefier. The cold fluid enters a counter-flow liquefier, at -20ºC and 1.01 bar.

Table 45 – Considered Values and Heat Transfer for Liquefier.

Case	Scenario 3
Liquefier	**LF-201**
$\boldsymbol{Flow\ Rate}_{\boldsymbol{hot}}$ (kg/h)	273.99
$\boldsymbol{Flow\ Rate}_{\boldsymbol{cold}}$ (m^3/h)	1.5
$\boldsymbol{Flow\ Rate}_{\boldsymbol{cold}}$ (kg/h)	1,712
$\boldsymbol{\dot{m}_{hot}}$ (kg/s)	0.08
$\boldsymbol{C_{p,hot}}$ (kJ/kg ºC)	0.892
$\boldsymbol{C_{hot}}$ (kW/ºC)	**0.07**
$\boldsymbol{\dot{m}_{cold}}$ (kg/s)	0.475
$\boldsymbol{C_{p,cold}}$ (kJ/kg ºC)	2.18
$\boldsymbol{C_{cold}}$ (kW/ºC)	1.03
$\boldsymbol{C_{min}}$ (kW/ºC)	**0.07**
$\boldsymbol{T_{hot,in}}$ (ºC)	13.4
$\boldsymbol{T_{cold,in}}$ (ºC)	-20
$\Delta\boldsymbol{T_{max}}$ (ºC)	33
$\boldsymbol{\dot{Q}_{max}}$ (kW)	2.27
$\boldsymbol{\dot{Q}}$ **(kW)**	**1.87**
$\boldsymbol{T_{hot,out}}$ (ºC)	-14.2
$\boldsymbol{T_{cold,out}}$ (ºC)	-18.2

In Table 45, flow rate of the cold fluid is assumed since it can manipulate the outlet temperature of this fluid, which should not be too close to the outlet temperature of the hot stream, so heat transfer can occur. Also, it is considered a heat transfer rate ($\dot{Q}$) below the maximum heat transfer rate ($\dot{Q}_{max}$) since it can manipulate the outlet temperature of the hot fluid, which has to be -14ºC.

To convert the flow rate of the cold fluid it is used the mass density of ethylene glycol, which is obtained with Aspen Plus software program (Appendix II, Table 88). As well, the specific heats of each gas and liquid compounds are obtained (Appendix II, Table 89). To calculate the specific heat of total waste gas it is taken into account the quantity (v/v %) that each gas compound represents in the total air.

- **Dimensioning**

Table 46 shows the values used for calculation of heat transfer areas.

Table 46 – Heat Transfer Area for Liquefier.

Case	Scenario 3
Liquefier	**LF-201**
T_{in} (ºC)	13.4
T_{out} (ºC)	-14.2
t_{in} (ºC)	-20
t_{out} (ºC)	-18.2
ΔT_{mean} (ºC)	15.2
$\dot{Q}$ (W)	1,870.0
U (W/m^2 ºC)	50
A (m^2)	**2.5**

For the liquefaction unit it is used an approximate overall heat transfer coefficient (U) (Annex IV, Figure 55).

Table 47 shows the values used for calculation of number of tubes.

Table 47 – Number of Tubes in the Shell, for Liquefier.

Case	Scenario 3
Liquefier	**LF-201**
d_o (m)	0.025
d_i (m)	0.0186
w (m)	0.0032
π	3.14
L (m)	7.32
A_s (m^2)	0.575
A (m^2)	2.5
n_{tubes}	**4**

- **Shell Diameter**

Table 48 shows the values used for calculation of minimum shell diameter.

Table 48 – Minimum Shell Diameter, for Liquefier.

Case	Scenario 3
Liquefier	**LF-201**
d_o (m)	0.025
PR	1.25
$A_{tube,triangular}$ (m^2)	0.000846
π	3.14
n_{tubes}	4
D_{tight} (m)	0.068
n_p	1
$A_{corrected}$ (m^2)	0.004
$D_{s,\ min}$ (m)	**0.118**

- **Shell Baffles**

Table 49 shows the values used for calculation of number of baffles.

Table 49 – Minimum Number of Baffles, for Liquefier.

Case	Scenario 3
Liquefier	**LF-201**
$D_{s,}$ (m)	0.118
$L_{b,min}$ (m)	0.024
L (m)	7.32
Baffle cut	20%
$N_{b,min}$	**310**

3.6.10 Storage Tanks

Storage tanks can store the liquefied compressed N_2O gas, at -14ºC and 44 bar.

Table 50 shows the volumes for each storage tank. It is considered at least 2 weeks of time for N_2O storing.

Table 50 – Storage Tank Volumes.

Case	Scenario 3	
Storage Tank	**ST – 201 A**	**ST – 201 B**
$Inlet\ Flow\ rate$ (m^3/h)	**0.04215**	**0.04215**
N_2O Storing (days)	**14**	**14**
V (m^3)	**14.2**	**14.2**

Storage tanks are supplied with nitrogen gas to create an inert atmosphere in there. Nitrogen gas quantity takes into account possible volume oscillations occurring in the year. Thus, for nitrogen gas it is assumed a volume which is 10 times the storage tank volume (Table 51). The pressure 2 bar is also assumed.

Table 51 – Nitrogen gas in Storage Tanks.

Case	**Scenario 3**	
Storage Tank	**ST – 201 A**	**ST – 201 B**
N_2 gas (m^3 / year)	142	142
P (bar)	2	2
N_2 density, ρ (kg/m^3)	2.28	2.28
N_2 gas (kg / year)	**324**	**324**

Mass density of N_2 gas at 2 bar is obtained using Aspen Plus software program (Appendix II, Table 88).

3.6.11 Instrumentation and Control Engineering

Instrumentation is defined as the art and science of measurement and control of process variables within a production or manufacturing area. The process variables used in industries are Level, Pressure, Temperature, Humidity, Flow, pH, Force, Speed etc. Control engineering or control systems engineering is the engineering discipline that applies control theory to design systems with desired behaviors.

The practice uses sensors to measure the output performance of the device being controlled and those measurements can be used to give feedback to the input actuators that can make corrections toward desired performance. When a device is designed to perform without the need of human inputs for correction it is called automatic control (such as cruise control for regulating a car's speed).

4. Economic Analysis for N_2O Recovery

In the present study, it is considered 350 days (8400 h) of annual operation time. It is taken into account 15 days left per year for time plant start-up preparation, holidays, supervisions, equipment maintenance and also possible cleaning operations. A brief summary is presented in Table 52.

Table 52 – N_2O Purification Operation Time.

Case	Scenario 1	Scenario 2	Scenario 3
N_2O Purification	24%	24%	99.7%
Pressure	Vacuum system	Up to 3 bar	Up to 44 bar
Purpose	Biogas Pre-treatment	Biogas pre-treatment	Additional Revenue
Final N_2O Purification	68%	68%	99.7%
Objective	**Biogas Combustion**	**Biogas Combustion**	**Selling N_2O**
N_2O Gas Production (kg/h)	143.9	143.9	81.62
Operation Time (h)	8400	8400	8400
N_2O Gas Production (ton/yr)	**1,208.7**	**1,208.7**	**685.6**

4.1 Base Equipment Cost

In the present study, it is necessary to update equipment costs for the current year (2016). Costs can be calculated using Equation 49, where A and B stand for the current and previously year, respectively.

$$Cost_{at\ A} = Cost_{at\ B}\left(\frac{Index_{at\ A}}{Index_{at\ B}}\right)$$

Equation 49 – Equipment Update Cost.

The preliminary value for January 2015 CEPCI[21] (most recent available) sits only 0.11% higher than the year-earlier value (2014), which was calculated at 576.1. This total is higher than the annual value for the previous year (567.3), but still below the 2012 annual average (584.6) [86].

Table 53 shows CE Plant Cost Index in recent years.

Table 53 – CE Plant Cost Index (*CEPCI*) [86].

Annual Average	2012	2013	2014	2015/2016
Index	**584.6**	**567.3**	**576.1**	**576.73**

[21] Chemical Engineering Plant Cost Index

The considered total cost for base equipment, in each case scenario, is presented in Table 54. In Table 90 (Appendix III) is presented the prices for base equipment, individually.

Table 54 – Base Equipment Cost (Appendix III, Table 90).

Case	Scenario 1	Scenario 2	Scenario 3
Total	**76,740 €**	**238,743 €**	**1,427,068 €**

4.2 Total Fixed Investment (CAPEX)

There are other several costs that must be taken into account for total investment, beyond base equipment costs. These are called direct costs and each account for 5% estimation on base equipment cost, in the present study. The estimated total fixed investment is presented in Table 55.

Table 55 – Capital Expenditure (*CAPEX*).

Direct Costs		Scenario 1	Scenario 2	Scenario 3
base equipment cost	-	76,740 €	238,743 €	1,427,068 €
base equipment delivery + installation	5%	3,837 €	11,937 €	71,353 €
pipelines	5%	3,837 €	11,937 €	71,353 €
instrumentation and control	5%	3,837 €	11,937 €	71,353 €
electrical installations	5%	3,837 €	11,937 €	71,353 €
thermal insulations	5%	3,837 €	11,937 €	71,353 €
TOTAL Investment		95,925 €	298,429 €	1,855,189 €

In order to estimate the direct costs there are some specific percentage values on base equipment cost, which are primarily focused in case situations of industrial plant constructions:

- Base equipment delivery and installation (35% – 45%)
- Pipelines: solids (10%), solids and fluids (30%), fluids (65%)
- Instrumentation and control (5% – 30%)
- Electrical installations (10% – 15%)
- Thermal insulations (8% – 10%)

[39]

In the present study, the three case scenarios are only situations of fitting a section to the wastewater treatment plant. Thus, the 5% estimation on base equipment cost for direct costs calculation is underestimated.

Also, it is important to ensure capital resources for possible unforeseen situations, such as changes in infrastructures (chapter 2.12). If the biological tank(s) are open air zones, then once N_2O is maximized the tank(s) must be completely covered (e.g. using one or more campanulas) to ensure that no waste gas goes into the atmosphere. Handling infrastructures depend on area dimensions of local biological tank(s), as such, total fixed investment can be overestimated. Nevertheless, these theoretical costs are an approach to the expected real costs.

4.3 Investment Plan

- **Assumptions**

N_2O plant recovery will have its production beginning on 2018, and operating for 10 years. Installation of equipment and ground's preparation will start in 2017, which matches for the investment year.

- **The French System**

It is considered to use a bank loan for the capital expenditure, followed by the French system which is characteristic for obtaining a fixed provision throughout the repayment period (amortization), with a constant interest rate of 7% [87]. Equations 50, 51 and 52 are useful to estimate the investment plan of each case scenario.

$$\boldsymbol{j_n = D_{n-1} \times i}$$

Equation 50 – Mid-term Interest Fee [88].

$\boldsymbol{j_n}$: Mid-term interest fee, during the period n
$\boldsymbol{D_{n-1}}$: Bank Loan, in the previous period n
$\boldsymbol{i}$: Constant interest rate (i=7%)

$$\boldsymbol{P_{annual} = \frac{D_0 \times i}{1 - (1 + i)^{-n}}}$$

Equation 51 – Annual Provision [88].

$\boldsymbol{D_0}$: Bank Loan, in the first year of investment
$\boldsymbol{n}$: Number of time periods (n=10)

$$\boldsymbol{m_n = P_{annual} - j_n}$$

Equation 52 – Amortization [88].

$\boldsymbol{m_n}$: Amortization, during the period n

The investment plan of each case scenario is presented in Tables 56, 57 and 58, respectively.

Table 56 – Investment Plan, in case of Scenario 1.

Case Scenario 1					
Year	n	Mid-term Interest Fees	Amortizations	Annual Provisions	Bank Loans
2017	-	**- €**	- €	- €	**95,925 €**
2018	1	6,715 €	6,943 €	13,658 €	88,982 €
2019	2	6,229 €	7,429 €	13,658 €	81,553 €
2020	3	5,709 €	7,949 €	13,658 €	73,604 €
2021	4	5,152 €	8,505 €	13,658 €	65,099 €
2022	5	4,557 €	9,101 €	13,658 €	55,998 €
2023	6	3,920 €	9,738 €	13,658 €	46,261 €
2024	7	3,238 €	10,419 €	13,658 €	35,842 €
2025	8	2,509 €	11,149 €	13,658 €	24,693 €
2026	9	1,729 €	11,929 €	13,658 €	12,764 €
2027	10	893 €	12,764 €	13,658 €	0 €
	TOTAL	40,650 €	95,925 €	136,575 €	

Table 57 – Investment Plan, in case of Scenario 2.

Case Scenario 2					
Year	n	Mid-term Interest Fees	Amortizations	Annual Provisions	Bank Loans
2017	-	**- €**	- €	- €	**298,429 €**
2018	1	20,890 €	21,600 €	42,490 €	276,829 €
2019	2	19,378 €	23,112 €	42,490 €	253,718 €
2020	3	17,760 €	24,729 €	42,490 €	228,989 €
2021	4	16,029 €	26,460 €	42,490 €	202,528 €
2022	5	14,177 €	28,313 €	42,490 €	174,216 €
2023	6	12,195 €	30,294 €	42,490 €	143,921 €
2024	7	10,074 €	32,415 €	42,490 €	111,506 €
2025	8	7,805 €	34,684 €	42,490 €	76,822 €
2026	9	5,378 €	37,112 €	42,490 €	39,710 €
2027	10	2,780 €	39,710 €	42,490 €	0 €
	TOTAL	126,467 €	298,429 €	424,896 €	

Table 58 – Investment Plan, in case of Scenario 3.

Case Scenario 3					
Year	n	Mid-term Interest Fees	Amortizations	Annual Provisions	Bank Loans
2017	-	**- €**	- €	- €	**1,855,189 €**
2018	1	129,863 €	134,274 €	264,137 €	1,720,915 €
2019	2	120,464 €	143,673 €	264,137 €	1,577,242 €
2020	3	110,407 €	153,730 €	264,137 €	1,423,511 €
2021	4	99,646 €	164,491 €	264,137 €	1,259,020 €
2022	5	88,131 €	176,006 €	264,137 €	1,083,014 €
2023	6	75,811 €	188,326 €	264,137 €	894,688 €
2024	7	62,628 €	201,509 €	264,137 €	693,179 €
2025	8	48,523 €	215,615 €	264,137 €	477,565 €
2026	9	33,430 €	230,708 €	264,137 €	246,857 €
2027	10	17,280 €	246,857 €	264,137 €	0 €
	TOTAL	786,183 €	1,855,189 €	2,641,371 €	

4.4 Total Operational Costs, OPEX

Production costs comprise all costs of production, mainly raw materials, salary payments, operational utilities and local tax profits.

- **Operational Utilities**

Several utilities, associated with different functions, are required to the production facility, such as electricity, activated carbon, glycol water, etc. The electricity of instrumentation and control can vary between 5% – 20% on total electricity [39].

Electricity prices for industrial consumers in Portugal are 0.0989 € per kWh (most recent available, in 2015) [89].

Membrane roll prices have already been calculated (Appendix III, Table 90), and these rolls must be replaced every 3 years (chapter 3.6.5).

In case of scenario 1, membrane rolls and electricity are the main operational utilities. The estimated price for electricity is present in Table 59. Instrumentation and control account for 5% estimation on total power of vacuum pumps.

Table 59 – Electricity Costs, in case of Scenario 1.

Utility	Reference		Total Power (W)	kW	kWh	€/kWh	€/year
Electricity	Vacuum Pumps	VP - 101 A/B/C/D	3,981.7	3.98	33447	0.0989	3,308 €
		VP - 102 A/B/C/D	1,960.3	1.960	16466		1,629 €
						TOTAL	4,936 €
	Instrumentation & Control			5%			247 €
						TOTAL	5,183 €

In case of scenario 2, membrane rolls and electricity are also the main operational utilities. The estimated price for electricity is present in Table 60. Instrumentation and control account for 5% estimation on total power of compressor and hydraulic pumps.

Table 60 – Electricity Costs, in case of Scenario 2.

Utility	Reference		Total Power (W)	kW	kWh	€/kWh	€/year
Electricity	Hydraulic Pumps	P - 101 A/B	10.2	0.01	86	0.0989	8.5 €
		P - 102 A/B	1.7	0.0017	14		1.4 €
	Compressor	C - 101	361,560	362	3,037,104		300,370 €
						TOTAL	300,379 €
	Instrumentation & Control			5%			15,019 €
						TOTAL	315,398 €

In case of scenario 3, the main operational utilities are membrane rolls, electricity, activated carbon and regeneration air for adsorption columns, ethylene glycol for the liquefier and nitrogen gas for storage tanks. The estimated price for electricity is present in Table 61. Instrumentation and control account for 15% estimation on total power of compressors and hydraulic pumps, once it also has to be considered the energy of section 200 (N_2O purification up to 99,7%), for instrumentation and control.

Table 61 – Electricity Costs, in case of Scenario 3.

Utility	Reference		Total Power (W)	kW	kWh	€/kWh	€/year
Electricity	Hydraulic Pumps	P - 101 A/B	10.0	0.01	84	0.0989	8.3 €
		P - 102 A/B	11.0	0.011	92		9.1 €
		P - 103 A/B	1.7	0.0017	14		1.4 €
	Compressors	C - 101	1,114,000	1,114	9,357,600		925,467 €
		C - 102	698,000	698	5,863,200		579,870 €
						TOTAL	1,505,356 €
	Instrumentation & Control			15%			225,803 €
						TOTAL	1,731,159 €

Activated carbon prices have already been calculated (Appendix III, Table 90), and these adsorbents must be replaced every single year (chapter 3.6.7). Regeneration air, ethylene glycol and nitrogen gas is now going to be evaluated.

Utility estimates are often complicated because they depend on both inflation and energy costs. This simplified approach offers a two-factor utility-cost equation (Equation 53) and the relevant coefficients for the process utilities (Table 62).

$$\boldsymbol{C_{S,u} = a\,(CEPCI) + b\,(C_{S,f})}$$

Equation 53 – Utility Price Estimation [90].

$C_{S,u}$: price of the utility per unit (\$/kJ, \$/ton, \$/m^3)

$a\ and\ b$: utility cost coefficients

$C_{S,f}$: price of the fuel (\$/GJ), which generated the utility

$CEPCI$: chemical engineering plant cost index

Table 62 – Utility Costs, in case of Scenario 3 (Annex V).

	Regeneration Air (compressed and dried)	Nitrogen Gas (N_2)	Ethylene Glycol (refrigerant)
a	0.0000728	0.00101	$1.8*10^{-8}$
b	0.0006238	0.0006238	$1.061*10^{-6}$
CEPCI (2016)	576.7	576.7	576.7
$C_{S,f}$ **($/GJ)**	12.48	12.48	12.48
$C_{S,u}$ **($/m^3)**	0.050	0.587	-
$C_{S,u}$ **($/kJ)**	-	-	$2.34*10^{-5}$
Flow rate (m^3/h)	213	-	-
Flow rate (m^3/yr)	1,792,513	284	-
Heat transfer rate (kW = kJ/s)	-	-	1.87
Heat transfer rate (kJ/yr)	-	-	56,548,800
$/yr	89,219	167	1,322
€/yr	**81,667**	**153**	**1,210**

- **Salary Payments**

In each case scenario, one labour is considered for instrumentation and control operations, with 1,161€ monthly, of estimated salary [91].

- **Maintenance/Repair Operations**

Maintenance estimates vary between 3% – 10% on total CAPEX, generally lower at the beginning and increased as time passes, since equipment is going to be degraded over time [39].

In each case scenario, maintenance and repair of base equipment account for 1% estimation on total CAPEX, every year. This is mainly due to the fact that Alcântara's WWTP already has a maintenance/repair team which can be used, and also the robustness of equipment that doesn't require many adjustments. Those include equipment not making noise or turbulence. In other words, equipment like pumps or compressors are going to be the only ones most repaired. Nevertheless, these theoretical costs are an approach to the expected real costs, and can be underestimated.

- **Total Operational Costs, OPEX**

Production costs of each case scenario are presented in Tables 63, 64 and 65, respectively.

Table 63 – Operational Expenditure (*OPEX*), in case of Scenario 1.

Case Scenario 1										
	1	2	3	4	5	6	7	8	9	10
Direct Costs	***2018***	***2019***	***2020***	***2021***	***2022***	***2023***	***2024***	***2025***	***2026***	***2027***
Raw Materials	- €	- €	- €	- €	- €	- €	- €	- €	- €	- €
Instrumentation & Control (1 Labour)	13,932 €	13,932 €	13,932 €	13,932 €	13,932 €	13,932 €	13,932 €	13,932 €	13,932 €	13,932 €
Electricity	5,183 €	5,183 €	5,183 €	5,183 €	5,183 €	5,183 €	5,183 €	5,183 €	5,183 €	5,183 €
Membrane: Cellulose Acetate	- €	- €	- €	3,073 €	- €	- €	- €	3,073 €	- €	- €
Maintenance/Repair	**1% 959 €**	**1% 959 €**	**1% 959 €**	**1% 959 €**	**1% 959 €**	**1% 959 €**	**1% 959 €**	**1% 959 €**	**1% 959 €**	**1% 959 €**
CAPEX Amortization	6,943 €	7,429 €	7,949 €	8,505 €	9,101 €	9,738 €	10,419 €	11,149 €	11,929 €	12,764 €
Patents & Royalties	- €	- €	- €	- €	- €	- €	- €	- €	- €	- €
TOTAL	**27,017 €**	**27,503 €**	**28,023 €**	**31,652 €**	**29,175 €**	**29,812 €**	**30,494 €**	**34,296 €**	**32,003 €**	**32,838 €**
General Costs										
Administration	- €	- €	- €	- €	- €	- €	- €	- €	- €	- €
Investigation & Development	- €	- €	- €	- €	- €	- €	- €	- €	- €	- €
Financial Charges	6,715 €	6,229 €	5,709 €	5,152 €	4,557 €	3,920 €	3,238 €	2,509 €	1,729 €	893 €
Insurance	- €	- €	- €	- €	- €	- €	- €	- €	- €	- €
Local Tax Profit	- €	- €	- €	- €	- €	- €	- €	- €	- €	- €
TOTAL	**6,715 €**	**6,229 €**	**5,709 €**	**5,152 €**	**4,557 €**	**3,920 €**	**3,238 €**	**2,509 €**	**1,729 €**	**893 €**
OPEX costs	**33,732 €**	**33,732 €**	**33,732 €**	**36,805 €**	**33,732 €**	**33,732 €**	**33,732 €**	**36,805 €**	**33,732 €**	**33,732 €**

Table 64 – Operational Expenditure (*OPEX*), in case of Scenario 2.

Case Scenario 2										
	1	2	3	4	5	6	7	8	9	10
Direct Costs	***2018***	***2019***	***2020***	***2021***	***2022***	***2023***	***2024***	***2025***	***2026***	***2027***
Raw Materials	- €	- €	- €	- €	- €	- €	- €	- €	- €	- €
Instrumentation & Control (1 Labour)	13,932 €	13,932 €	13,932 €	13,932 €	13,932 €	13,932 €	13,932 €	13,932 €	13,932 €	13,932 €
Electricity	315,398 €	315,398 €	315,398 €	315,398 €	315,398 €	315,398 €	315,398 €	315,398 €	315,398 €	315,398 €
Membrane: Cellulose Acetate	- €	- €	- €	623 €	- €	- €	- €	623 €	- €	- €
Maintenance/Repair	**1% 2,984 €**	**1% 2,984 €**	**1% 2,984 €**	**1% 2,984 €**	**1% 2,984 €**	**1% 2,984 €**	**1% 2,984 €**	**1% 2,984 €**	**1% 2,984 €**	**1% 2,984 €**
CAPEX Amortization	21,600 €	23,112 €	24,729 €	26,460 €	28,313 €	30,294 €	32,415 €	34,684 €	37,112 €	39,710 €
Patents & Royalties	- €	- €	- €	- €	- €	- €	- €	- €	- €	- €
TOTAL	**353,914 €**	**355,426 €**	**357,044 €**	**359,398 €**	**360,627 €**	**362,609 €**	**364,730 €**	**367,622 €**	**369,427 €**	**372,025 €**
General Costs										
Administration	- €	- €	- €	- €	- €	- €	- €	- €	- €	- €
Investigation & Development	- €	- €	- €	- €	- €	- €	- €	- €	- €	- €
Financial Charges	20,890 €	19,378 €	17,760 €	16,029 €	14,177 €	12,195 €	10,074 €	7,805 €	5,378 €	2,780 €
Insurance	- €	- €	- €	- €	- €	- €	- €	- €	- €	- €
Local Tax Profit	- €	- €	- €	- €	- €	- €	- €	- €	- €	- €
TOTAL	**20,890 €**	**19,378 €**	**17,760 €**	**16,029 €**	**14,177 €**	**12,195 €**	**10,074 €**	**7,805 €**	**5,378 €**	**2,780 €**
OPEX costs	**374,804 €**	**374,804 €**	**374,804 €**	**375,427 €**	**374,804 €**	**374,804 €**	**374,804 €**	**375,427 €**	**374,804 €**	**374,804 €**

Table 65 – Operational Expenditure (*OPEX*), in case of Scenario 3.

	Case Scenario 3									
	1	2	3	4	5	6	7	8	9	10
Direct Costs	***2018***	***2019***	***2020***	***2021***	***2022***	***2023***	***2024***	***2025***	***2026***	***2027***
Raw Materials	- €	- €	- €	- €	- €	- €	- €	- €	- €	- €
Instrumentation & Control (1 Labour)	13,932 €	13,932 €	13,932 €	13,932 €	13,932 €	13,932 €	13,932 €	13,932 €	13,932 €	13,932 €
Electricity	1,731,159 €	1,731,159 €	1,731,159 €	1,731,159 €	1,731,159 €	1,731,159 €	1,731,159 €	1,731,159 €	1,731,159 €	1,731,159 €
Membrane: Cellulose Acetate	- €	- €	- €	477 €	- €	- €	- €	477 €	- €	- €
Ethylene glycol: C2H6O2	1,210 €	1,210 €	1,210 €	1,210 €	1,210 €	1,210 €	1,210 €	1,210 €	1,210 €	1,210 €
Adsorption Columns: Regeneration Air	81,667 €	81,667 €	81,667 €	81,667 €	81,667 €	81,667 €	81,667 €	81,667 €	81,667 €	81,667 €
Storage Tanks: N2	153 €	153 €	153 €	153 €	153 €	153 €	153 €	153 €	153 €	153 €
Granular Activated Carbon	- €	3,639 €	3,639 €	3,639 €	3,639 €	3,639 €	3,639 €	3,639 €	3,639 €	3,639 €
Maintenance/Repair	**1%** **18,552 €**	**1%** **18,552 €**	**1%** **18,552 €**	**1%** **18,552 €**	**1%** **18,552 €**	**1%** **18,552 €**	**1%** **18,552 €**	**1%** **18,552 €**	**1%** **18,552 €**	**1%** **18,552 €**
CAPEX Amortization	134,274 €	143,673 €	153,730 €	164,491 €	176,006 €	188,326 €	201,509 €	215,615 €	230,708 €	246,857 €
Patents & Royalties	- €	- €	- €	- €	- €	- €	- €	- €	- €	- €
TOTAL	**1,980,947 €**	**1,993,984 €**	**2,004,042 €**	**2,015,280 €**	**2,026,317 €**	**2,038,637 €**	**2,051,820 €**	**2,066,403 €**	**2,081,019 €**	**2,097,168 €**
General Costs										
Administration	- €	- €	- €	- €	- €	- €	- €	- €	- €	- €
Investigation & Development	- €	- €	- €	- €	- €	- €	- €	- €	- €	- €
Financial Charges	129,863 €	120,464 €	110,407 €	99,646 €	88,131 €	75,811 €	62,628 €	48,523 €	33,430 €	17,280 €
Insurance	- €	- €	- €	- €	- €	- €	- €	- €	- €	- €
Local Tax Profit	- €	- €	- €	- €	- €	- €	- €	- €	- €	- €
TOTAL	**129,863 €**	**120,464 €**	**110,407 €**	**99,646 €**	**88,131 €**	**75,811 €**	**62,628 €**	**48,523 €**	**33,430 €**	**17,280 €**
OPEX costs	**2,110,810 €**	**2,114,448 €**	**2,114,448 €**	**2,114,926 €**	**2,114,448 €**	**2,114,448 €**	**2,114,448 €**	**2,114,926 €**	**2,114,448 €**	**2,114,448 €**

In general costs, administration, investigation and development refer to salary payments and these costs are neglected since Alcântara's WWTP already has people working in this area thus no need of additional capital resources is required. As for insurance and local tax profit, Alcântara's WWTP also settles these costs and, therefore, are neglected.

The cost analysis of N_2O doesn't include the costs of filling, storing, maintaining, or delivering the cylinders. These costs vary geographically and depend on the volume requested by the costumer, the tank size, and the distance from the manufacturing site to the customer.

4.5 Revenues

- **Electrical Energy**

In the present study, it is considered 30% for energy recovery through biogas combustion (chapter 2.9). The return value is 0.10 € per kWh of recovered energy in Alcantara's WWTP, and the heat of reaction is presented in Table 66.

Table 66 – Energy Recovery, in case scenarios 1 and 2 (chapter 2.10).

Case Scenarios 1 and 2		
Biogas Combustion		
Return Value	**0.1 €/kWh**	
CH4 + N2O	1,219	kJ/mol
Recovery (30%)	366	kJ/mol

Table 67 shows N_2O annual production. For N_2O mole conversion, it is used its molecular weight (Appendix II, Table 87).

Table 67 – N_2O Annual Production, in case scenarios 1 and 2.

Case Scenario 1		
N2O (24%)	143.93	kg/h
	80	m3/h
N2O (24%)	1,209	ton/yr
	672,026	m3/yr
	27,468,847	mol/yr

Case Scenario 2		
N2O (24%)	27.03	m3/h
	143.93	kg/h
N2O (24%)	1,209	ton/yr
	227,086	m3/yr
	27,468,847	mol/yr

Table 68 shows N_2O production cost per year.

Table 68 – N_2O Production Cost, in case scenarios 1 and 2.

Case Scenario 1	*2018*	*2019*	*2020*	*2021*	*2022*	*2023*	*2024*	*2025*	*2026*	*2027*	
OPEX	33,732 €	33,732 €	33,732 €	36,805 €	33,732 €	33,732 €	33,732 €	36,805 €	33,732 €	33,732 €	€/year
N2O Gas Production Cost	0.028 €	0.028 €	0.028 €	0.030 €	0.028 €	0.028 €	0.028 €	0.030 €	0.028 €	0.028 €	€/kg
	0.050 €	0.050 €	0.050 €	0.055 €	0.050 €	0.050 €	0.050 €	0.055 €	0.050 €	0.050 €	€/m3

Case Scenario 2	*2018*	*2019*	*2020*	*2021*	*2022*	*2023*	*2024*	*2025*	*2026*	*2027*	
OPEX	374,804 €	374,804 €	374,804 €	375,427 €	374,804 €	374,804 €	374,804 €	375,427 €	374,804 €	374,804 €	€/year
N2O Gas Production Cost	0.310 €	0.310 €	0.310 €	0.311 €	0.310 €	0.310 €	0.310 €	0.311 €	0.310 €	0.310 €	€/kg
	1.65 €	1.65 €	1.65 €	1.65 €	1.65 €	1.65 €	1.65 €	1.65 €	1.65 €	1.65 €	€/m3

Using Tables 66 and 67, revenues can be calculated (Table 69).

Table 69 – Revenues, in case scenarios 1 and 2.

Case Scenarios 1 and 2		
Annual Heat Production		
Generated Heat	10,045,357,523	kJ/year
	10,045	GJ/year
	332	kW = kJ/s
	2,790,377	kWh
Annual Income	**279,038 € /yr**	

- **Selling N_2O**

In case of scenario 3, annual production of N_2O is presented in Table 70.

Table 70 – N_2O Annual Production, in case scenario 3.

Case Scenario 3		
Annual Production		
TOTAL (N2O 99.7%)	0.0843	m3/h
	81.72	kg/h
TOTAL (N2O 99.7%)	686,429	kg/yr
	686	ton/yr
	708	m3/yr

Table 71 shows the production cost of N_2O per year.

Table 71 – N_2O Production Cost, in case scenarios 3.

Case Scenario 3	*2018*	*2019*	*2020*	*2021*	*2022*	*2023*	*2024*	*2025*	*2026*	*2027*	
OPEX	2,110,810 €	2,114,448 €	2,114,448 €	2,114,926 €	2,114,448 €	2,114,448 €	2,114,448 €	2,114,926 €	2,114,448 €	2,114,448 €	€/year
N2O Gas	3.08 €	3.08 €	3.08 €	3.08 €	3.08 €	3.08 €	3.08 €	3.08 €	3.08 €	3.08 €	€/kg
Production Cost	2,981.1 €	2,986.2 €	2,986.2 €	2,986.9 €	2,986.2 €	2,986.2 €	2,986.2 €	2,986.9 €	2,986.2 €	2,986.2 €	€/m3

It can be considered a value between 12 – 15€ per kg of N_2O, for cylinders with 35 kg of capacity (chapter 3.4). In the present study, it is estimated 4 € per kg for the selling product (N_2O). Therefore, revenues can be calculated (Table 72).

Table 72 – Revenues, in case scenario 3.

Case Scenario 3		
N2O Sales	4.0	€/kg
Annual Income	**2,745,718 €**	**/yr**

- **Thermal Energy**

Recovered generator heat can be used to dry the remaining digester solid for plant fertilizer, which can be sold for additional revenue for the WWTP (chapter 2.9). Heat exchangers of case scenarios 2 and 3 can be useful for heat generation (Table 73).

Table 73 – Heat Recovery, in case scenarios 2 and 3.

Case Scenario 2		
Annual Heat Recovery	**HE-101**	
Q	380	kW
Recovery (30%)	114	kW
Annual Heat	957,600	kWh

Case Scenario 3			
Annual Heat Recovery	**HE-101**	**HE-102**	
Q	400	278	kW
Recovery (30%)	120	83	kW
Annual Heat	1,008,000	700,560	kWh

4.6 Cash-flows

The **investment cash flows** or cash flows from investing activities, shows company's cash outflows and inflows related to the purchase and sale of investments [92].

The **exploration cash flows** refers to net return value of payments associated with the project operations [93].

Thus, **net cash flows** can be defined as the exploration cash flows minus the investment cash flows [93].

The **net present cash flows** refers to the update of net cash flows, associated with a constant rate of return (Equation 54) [93].

$$\boldsymbol{Net\ present\ cash\ flow} = \frac{\boldsymbol{C_n}}{(\boldsymbol{1}+\boldsymbol{k})^{\boldsymbol{n}}}$$

Equation 54 – Net Present Cash Flow [93].

$\boldsymbol{k}$: Constant rate of return (**k=7%**) [94]
$\boldsymbol{n}$: Number of time periods (n=1, 2... to 10)
$\boldsymbol{C_n}$: Net cash flow, during the period n

The **equity** of a company refers to the value that can be represented per year, after expenses and debts of the company have been paid.

In case of scenario 3, it is considered an estimated **tax profit** of 20% on gross return value, since N_2O has to be sold and in Portugal tax profit of selling products are expected to be around 20%, in 2018.

The **accumulated cash flows** can be calculated using Equation 55.

$$\boldsymbol{Accumulated\ cash\ flow} = \boldsymbol{Net\ present\ cash\ flow_n} + \boldsymbol{Accumulated\ cash\ flow_{n-1}}$$

Equation 55 – Accumulated Cash Flow [93].

$\boldsymbol{cash\ flow_n}$: Cash flow during the period n
$\boldsymbol{cash\ flow_{n-1}}$: Cash flow in the previous period n

Cash flows for each case scenario are presented in Tables 74, 75 and 76, respectively.

Table 74 – Cash-Flows, in Case of Scenario 1.

	Case Scenario 1										
	0	1	2	3	4	5	6	7	8	9	10
Cash-Flows	***2017***	***2018***	***2019***	***2020***	***2021***	***2022***	***2023***	***2024***	***2025***	***2026***	***2027***
1: Investment Cash-flows	95,925 €	- €	- €	- €	- €	- €	- €	- €	- €	- €	- €
2: Annual Incomes (Electrical Energy)	**- €**	**279,038 €**	**279,038 €**	**279,038 €**	**279,038 €**	**279,038 €**	**279,038 €**	**279,038 €**	**279,038 €**	**279,038 €**	**279,038 €**
3: OPEX costs	- €	33,732 €	33,732 €	33,732 €	36,805 €	33,732 €	33,732 €	33,732 €	36,805 €	33,732 €	33,732 €
4: Net Return Value (2-3)	**- €**	**245,306 €**	**245,306 €**	**245,306 €**	**242,233 €**	**245,306 €**	**245,306 €**	**245,306 €**	**242,233 €**	**245,306 €**	**245,306 €**
5: CAPEX Amortization	- €	6,943 €	7,429 €	7,949 €	8,505 €	9,101 €	9,738 €	10,419 €	11,149 €	11,929 €	12,764 €
6: Financial Charges	- €	6,715 €	6,229 €	5,709 €	5,152 €	4,557 €	3,920 €	3,238 €	2,509 €	1,729 €	893 €
7: Equity	95,925 €	88,982 €	81,553 €	73,604 €	65,099 €	55,998 €	46,261 €	35,842 €	24,693 €	12,764 €	- €
8: Exploration Cash-flows (4+5+6)	**- €**	**258,963 €**	**258,963 €**	**258,963 €**	**255,891 €**	**258,963 €**	**258,963 €**	**258,963 €**	**255,891 €**	**258,963 €**	**258,963 €**
9: Net Cash-flows (8-1)	- 95,925 €	258,963 €	258,963 €	258,963 €	255,891 €	258,963 €	258,963 €	258,963 €	255,891 €	258,963 €	258,963 €
10: Net Present Cash-flows	- 95,925 €	242,022 €	226,189 €	211,391 €	195,218 €	184,637 €	172,558 €	161,269 €	148,931 €	140,859 €	131,644 €
11: Accumulated Cash-Flows	**- 95,925 €**	**146,097 €**	**372,286 €**	**583,677 €**	**778,895 €**	**963,532 €**	**1,136,090 €**	**1,297,359 €**	**1,446,290 €**	**1,587,149 €**	**1,718,792 €**

Table 75 – Cash-Flows, in Case of Scenario 2.

	Case Scenario 2										
	0	1	2	3	4	5	6	7	8	9	10
Cash-Flows	***2017***	***2018***	***2019***	***2020***	***2021***	***2022***	***2023***	***2024***	***2025***	***2026***	***2027***
1: Investment Cash-flows	298,429 €	- €	- €	- €	- €	- €	- €	- €	- €	- €	- €
2: Annual Incomes (Electrical Energy)	**- €**	**279,038 €**	**279,038 €**	**279,038 €**	**279,038 €**	**279,038 €**	**279,038 €**	**279,038 €**	**279,038 €**	**279,038 €**	**279,038 €**
3: OPEX costs	- €	374,804 €	374,804 €	374,804 €	375,427 €	374,804 €	374,804 €	374,804 €	375,427 €	374,804 €	374,804 €
4: Net Return Value (2-3)	**- €**	**- 95,767 €**	**- 95,767 €**	**- 95,767 €**	**- 96,389 €**	**- 95,767 €**	**- 95,767 €**	**- 95,767 €**	**- 96,389 €**	**- 95,767 €**	**- 95,767 €**
5: CAPEX Amortization	- €	21,600 €	23,112 €	24,729 €	26,460 €	28,313 €	30,294 €	32,415 €	34,684 €	37,112 €	39,710 €
6: Financial Charges	- €	20,890 €	19,378 €	17,760 €	16,029 €	14,177 €	12,195 €	10,074 €	7,805 €	5,378 €	2,780 €
7: Equity	298,429 €	276,829 €	253,718 €	228,989 €	202,528 €	174,216 €	143,921 €	111,506 €	76,822 €	39,710 €	- €
8: Exploration Cash-flows (4+5+6)	**- €**	**- 53,277 €**	**- 53,277 €**	**- 53,277 €**	**- 53,900 €**	**- 53,277 €**	**- 53,277 €**	**- 53,277 €**	**- 53,900 €**	**- 53,277 €**	**- 53,277 €**
9: Net Cash-flows (8-1)	- 298,429 €	- 53,277 €	- 53,277 €	- 53,277 €	- 53,900 €	- 53,277 €	- 53,277 €	- 53,277 €	- 53,900 €	- 53,277 €	- 53,277 €
10: Net Present Cash-flows	- 298,429 €	- 49,792 €	- 46,534 €	- 43,490 €	- 41,120 €	- 37,986 €	- 35,501 €	- 33,178 €	- 31,370 €	- 28,979 €	- 27,083 €
11: Accumulated Cash-Flows	**- 298,429 €**	**- 348,221 €**	**- 394,755 €**	**- 438,245 €**	**- 479,365 €**	**- 517,350 €**	**- 552,851 €**	**- 586,029 €**	**- 617,399 €**	**- 646,379 €**	**- 673,462 €**

Table 76 – Cash-Flows, in Case of Scenario 3.

	Case Scenario 3										
	0	1	2	3	4	5	6	7	8	9	10
Cash-Flows	***2017***	***2018***	***2019***	***2020***	***2021***	***2022***	***2023***	***2024***	***2025***	***2026***	***2027***
1: Investment Cash-flows	1,855,189 €	- €	- €	- €	- €	- €	- €	- €	- €	- €	- €
2: Annual Incomes (Sales)	**- €**	**2,745,718 €**	**2,745,718 €**	**2,745,718 €**	**2,745,718 €**	**2,745,718 €**	**2,745,718 €**	**2,745,718 €**	**2,745,718 €**	**2,745,718 €**	**2,745,718 €**
3: OPEX costs	- €	2,110,810 €	2,114,448 €	2,114,448 €	2,114,926 €	2,114,448 €	2,114,448 €	2,114,448 €	2,114,926 €	2,114,448 €	2,114,448 €
4: Gross Return Value (2-3)	- €	634,908 €	631,269 €	631,269 €	630,792 €	631,269 €	631,269 €	631,269 €	630,792 €	631,269 €	631,269 €
5: Tax Profit (20%)	- €	126,982 €	126,254 €	126,254 €	126,158 €	126,254 €	126,254 €	126,254 €	126,158 €	126,254 €	126,254 €
6: Net Return Value (4-5)	**- €**	**507,926 €**	**505,015 €**	**505,015 €**	**504,634 €**	**505,015 €**	**505,015 €**	**505,015 €**	**504,634 €**	**505,015 €**	**505,015 €**
7: CAPEX Amortization	- €	134,274 €	143,673 €	153,730 €	164,491 €	176,006 €	188,326 €	201,509 €	215,615 €	230,708 €	246,857 €
8: Financial Charges	- €	129,863 €	120,464 €	110,407 €	99,646 €	88,131 €	75,811 €	62,628 €	48,523 €	33,430 €	17,280 €
9: Equity	1,855,189 €	1,720,915 €	1,577,242 €	1,423,511 €	1,259,020 €	1,083,014 €	894,688 €	693,179 €	477,565 €	246,857 €	0 €
10: Exploration Cash-flows (6+7+8)	**- €**	**772,063 €**	**769,152 €**	**769,152 €**	**768,771 €**	**769,152 €**	**769,152 €**	**769,152 €**	**768,771 €**	**769,152 €**	**769,152 €**
11: Net Cash-Flows (10-1)	- 1,855,189 €	772,063 €	769,152 €	769,152 €	768,771 €	769,152 €	769,152 €	769,152 €	768,771 €	769,152 €	769,152 €
12: Net Present Cash-Flows	- 1,855,189 €	721,554 €	671,808 €	627,858 €	586,491 €	548,395 €	512,519 €	478,989 €	447,432 €	418,368 €	390,998 €
13: Accumulated Cash-Flows	**- 1,855,189 €**	**- 1,133,634 €**	**- 461,827 €**	**166,031 €**	**752,522 €**	**1,300,917 €**	**1,813,436 €**	**2,292,426 €**	**2,739,857 €**	**3,158,225 €**	**3,549,223 €**

4.7 Analysis of Economic Profitability

The **payback period** is the length of time required to recover the cost of an investment. It's an important determinant of whether to undertake the position or project, as longer payback periods are typically not desirable for investment positions.

The **net present value (NPV)** is the difference between the present value of cash inflows and the present value of cash outflows (Equation 56). NPV is used in capital budgeting to analyze the profitability of a projected investment or project [95].

$$NPV = \sum_{n=1}^{N} \frac{C_n}{(1+k)^n} - C_0$$

Equation 56 – Net Present Value [95].

C_0: Total initial investment costs
k: Constant rate of return (**k=7%**)
n: Number of time periods (n=1, 2... to 10)
C_n: Net cash flow, during the period n

A positive net present value indicates that the projected earnings generated by a project or investment exceed the anticipated costs. Generally, an investment with a positive NPV will be a profitable one and one with a negative NPV will result in a net loss. This concept is the basis for the Net Present Value Rule, which dictates that the only investments that should be made are those with positive NPV values [95].

A brief summary is presented in Table 77.

Table 77 – Net Present Value Analysis.

	NPV
Acceptable Investment	> 0
Rejected Investment	< 0

The **internal rate of return (IRR)** is a metric used in capital budgeting measuring the profitability of potential investments. It's a discount rate that makes the net present value (NPV) of all cash flows from a particular project equal to zero (Figure 49) [96].

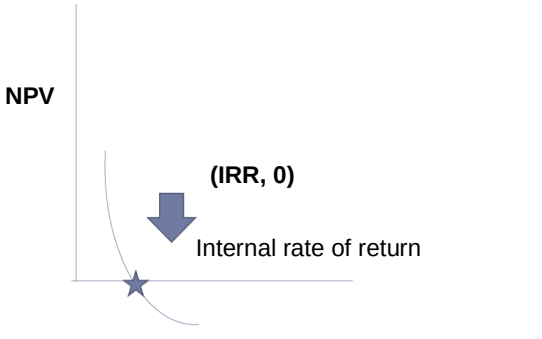

Figure 49 – Internal rate of return.

Generally, the higher a project's internal rate of return, the more desirable it is to undertake the project. IRR is uniform for investments of varying types and, as such, IRR can be used to rank multiple prospective projects which a firm is considering on a relatively even basis. Assuming the costs of investment are equal among the various projects, the project with the highest IRR would probably be considered the best and undertaken first [96].

In capital budgeting, the **hurdle rate** or the **minimum attractive/acceptable rate of return (MARR)** is the minimum rate that a company expects to earn when investing in a project. Hence the hurdle rate is also referred to as the company's required rate of return or target rate. In order for a project to be accepted, its internal rate of return must equal or exceed the hurdle rate [97].

A brief summary is presented in Table 78.

Table 78 – Hurdle Rate Analysis.

	Project	Business
IRR > Hurdle Rate	Economically feasible	Safe
IRR < Hurdle Rate	Economically not feasible	Unsafe

In the present study, hurdle rates account for 14% estimation, which is mainly the sum of the constant interest rate (i=7%) plus the constant rate of return (k=7%) [39].

Table 79 shows the profitability indicators for each case scenario.

Table 79 – Profitability Indicators.

Case	Scenario 1	Scenario 2	Scenario 3
Payback Period	4 months + 15 days	never	2 years + 9 months + 3 days
Net Present Value (NPV)	1,718,792 €	- 673,462 €	3,549,223 €
Internal Rate of Return (IRR)	269%	less than 7%	40%
Hurdle Rate	14%	14%	14%

4.8 Break-even Analysis

A break-even analysis is an analysis to determine the point at which revenue received equals the costs associated with receiving the revenue. Break-even analysis calculates what is known as a margin of safety, the amount that revenues exceed the break-even point. This is the amount that revenues can fall while still staying above the break-even point [98].

The break-even point for each case scenario is presented in Table 80, and graphically in Figures 50, 51 and 52, respectively.

Table 80 – Break-even point (Appendix IV, Tables 91, 92 and 93).

	Case Scenario 1	Case Scenario 2	Case Scenario 3
BEP (quantity, ton)	141.0	-	322.7
BEP (quantity)	11.7 %	-	47.0 %
BEP (value)	32,544 €	-	1,290,730 €

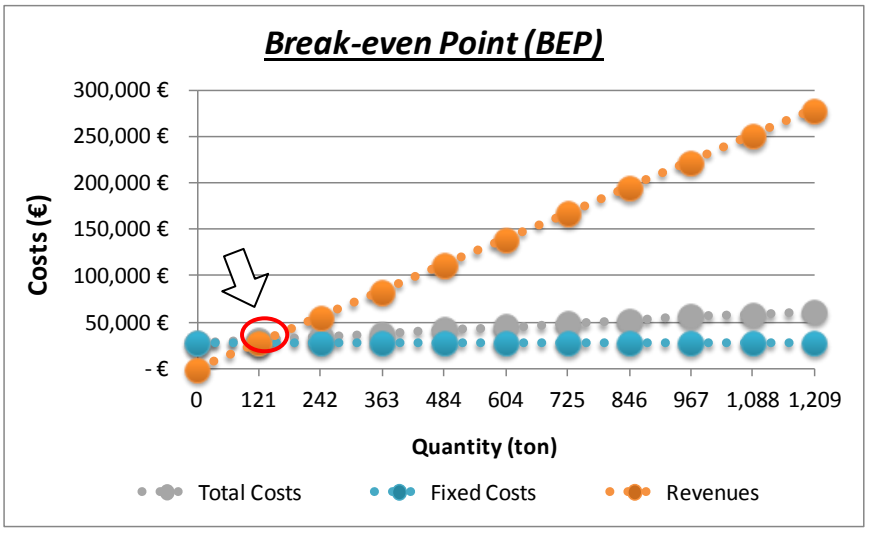

Figure 50 – Break-even Point, in Case of Scenario 1 (Appendix IV, Table 91).

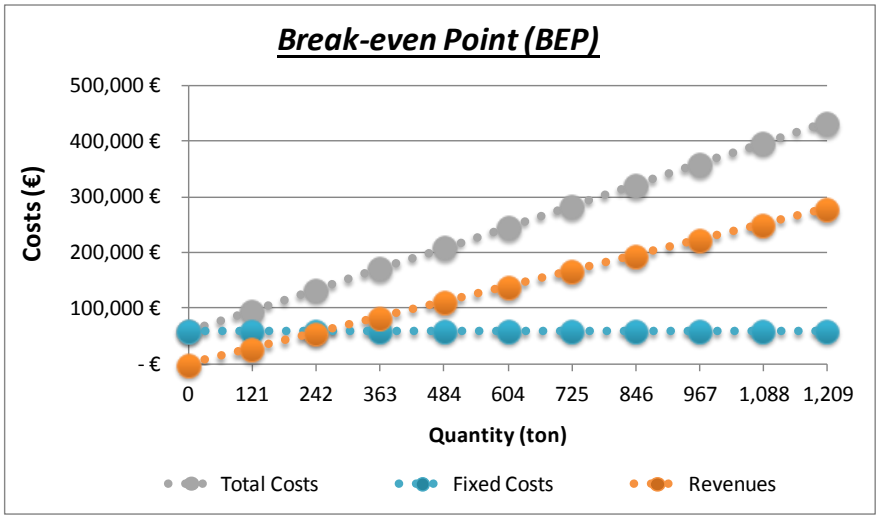

Figure 51 – Break-even Point, in Case of Scenario 2 (Appendix IV, Table 92).

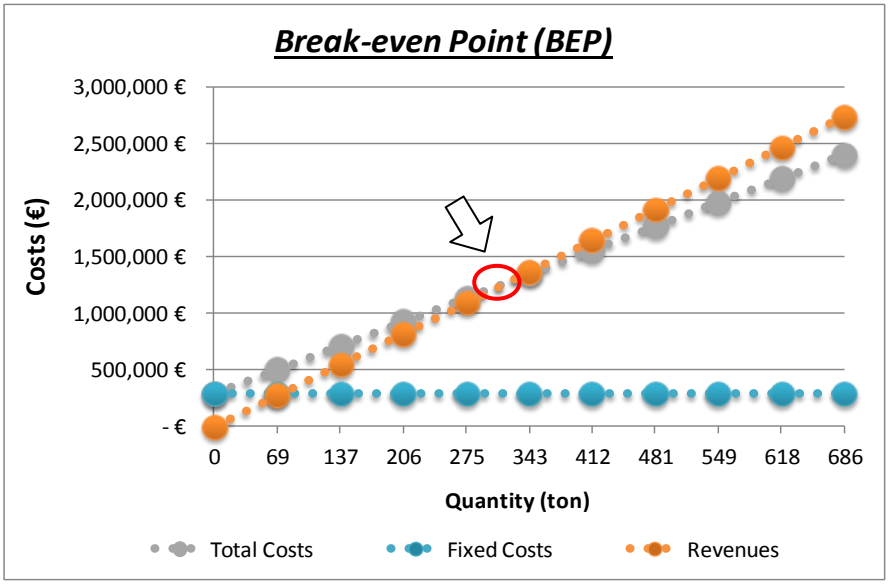

Figure 52 – Break-even Point, in Case of Scenario 3 (Appendix IV, Table 93).

4.9 Discussion of Results

In the first case scenario (Figure 50), assuming N_2O maximization in Alcântara's WWTP, a low BEP value (11.7%) was obtained which led to a small payback period (4 months and 15 days), of the initial CAPEX (Table 55). N_2O maximization increases the energy recovered in biogas combustion, and so higher revenues can be obtained, allowing an economic advantage to the WWTP. Nevertheless, the very small payback period suggests that lower N_2O emissions (below the assumed 50% emission factor) could also be economically advantageous, although future work is required to confirm this. Overall, this scenario appears to be very promising economically.

In the second case scenario (Figure 51), it can be noticed that, even assuming maximal N_2O production, the process is never profitable due to the higher purification costs.

In the third case scenario (Figure 52), it is obtained a BEP value of 47%, higher than the BEP value of the first case scenario, and so a long payback period (2 years, 9 months and 3 days). It should be noticed that this stands for the entire selling product (N_2O), which is always being sold (assumption). For this case, if N_2O production is not maximized in Alcântara's WWTP then lower revenues are obtained, the BEP value is going to be higher and a significantly higher degree of risk can be obtained for the project, allowing an economic disadvantage to the WWTP.

In Table 79, the first and third case scenarios seem to be the most attractive and acceptable projects (NPV > 0), for a possible investment opportunity. Also, these case scenarios are economically feasible projects (IRR > Hurdle Rate), meaning a safe business. Particularly, the first case scenario can be the most likely project to go ahead, with a significantly low degree of risk:

- **The first case scenario** is easier to be implemented, becomes quickly self-sustainable since revenue is certainly guaranteed and is the more economically safe project. Moreover, only one adaptation is going to be required in the biogas pretreatment, where N_2O is going to be sent (e.g introducing a 2-way flanged valve, allowing N_2O and biogas entrances). This can be assured by Alcântara's maintenance team, with no need of considerable additional costs.
- **The third case scenario** requires the use of much more equipment, the initial CAPEX and the OPEX values are considerable higher costs and the payback period is significantly dependent on N_2O sales, which may not always be able to be totally sold. This mainly depends on consumer demand.

Nevertheless, if the third case scenario is taken into consideration, then in a first step N_2O can be sold to the aerospace and auto racing industries (N_2O acting as an oxidant agent) and also to the chemical industry, in which N_2O is used in the production of NaN_3, the explosive agent that inflates an automobile air bag. If N_2O consumption is reasonable as it can cover all the purification costs (OPEX), then in a second step with some revenue entrances and, as such, after the estimated payback period, a distillation column may be purchased and so 99,999% of N_2O purity can be obtained. Thus, a significant portion of the N_2O market can possibly be reached. WWTPs would need capital resources to invest in the marketing section (e.g. image and safety issues from WWTPs) for high-purity applications, in order to compete with other industrial gas industries. Furthermore, industries such as medical applications and also food industries should likely be disregarded, since they are not a very good match with WWTPs.

5. Conclusions

In the present study, the following points can be concluded:

- If N_2O gas is recovered and purified in WWTPs, it can be possible to mitigate the release of N_2O to the atmosphere and a chance to have this by-product recognized as a saving potential also may be possible;

- If N_2O production is maximized in WWTPs, a chance to convert WWTPs into higher energy generators can be possible. N_2O increases the energy recovered in combustion reactions, as compared to conventional process which uses O_2 to oxidize CH_4, at WWTPs;

- If N_2O production is maximized in WWTPs, a chance to convert WWTPs into a business company also may be possible, using N_2O as the selling product. N_2O is commonly used to supercharge the engines of high performance vehicles (i.e. *Nitrox*) and as an oxidant in hybrid rocket motors in the aerospace industry;

- If N_2O production is maximized in WWTPs, safety strategies must be taken concerning its risks and hazards to the environment. In case the biological tank(s) are open air zones, then handling infrastructures to cover the entire N_2O capturing zone area, should be required. N_2O gas can't be allowed to escape, except via the suction tube (e.g. campanula).

- In 2015, the estimated N_2O emission factor for Alcântara's WWTP was 0.1297 g N_2O-N.(g N)$^{-1}$ (12.9% of the in-coming nitrogen). This value was higher than 0.035% proposed by IPCC 2006, but it is considered to be in the range typically observed at WWTPs, by Kampschreur et al. 2009 and Foley et. al. 2010.

- From literature review, SNDPR lab-studies have been experimentally demonstrated to be advantageous for N_2O accumulation. An emission factor around 50% of the in-coming nitrogen, can reasonably be expected from these SNDPR systems.

- The first case scenario can be the most likely project to go ahead, with a significantly low degree of risk: Payback period = 4 months + 15 days; Net present value = 1,718,792 €; Internal Rate of Return = 269%; Hurdle rate = 14%; Break-even point = 11.7%. It is expected that this process, if implemented in full-scale, would be very attractive indeed economically.

6. Future Work

In the future, WWTPs probably will need to sustain their own daily operational energy requirements, and counting on N_2O as a possible resource would aid in achieving this goal. Investigation will be required to optimize N_2O production in WWTPs (e.g. with SNDPR systems) and without compromising the performance of the wastewater treatment plant.

A market analysis would also be interesting to assess the actual consumption and production of N_2O gas, exports and imports (trade balances), and also prices on N_2O sales. Moreover, throughout a SWOT analysis, the strengths, weaknesses, opportunities and threats of a company could be identified, and adequate business strategies could be defined, for a WWTP.

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8. Appendix

8.1 Appendix I

Table 81 – Global GHGs Emissions.

World Resourses Institute [5]

	MT CO_2 Equivalent	
Year	***Total emissions (including LUCF)***	***Total emissions (excluding LUCF)***
1990	33,937	30,424
1991	33,281	30,648
1992	33,295	30,587
1993	33,409	30,693
1994	33,629	30,900
1995	34,310	31,559
1996	34,980	32,227
1997	35,413	32,508
1998	35,684	32,700
1999	35,829	32,970
2000	36,680	33,887
2001	37,366	34,257
2002	38,123	34,852
2003	39,449	36,152
2004	40,841	37,607
2005	42,001	38,782
2006	42,779	39,890
2007	43,916	41,135
2008	44,372	41,525
2009	44,003	41,237
2010	45,748	42,968
2011	46,906	44,191
2012	47,599	44,816

Table 82 – Total GHGs Emissions (including LUCF), of Top Emitters and from Selected Countries. World Resourses Institute [5]

	MT CO_2 Equivalent								
Year	***China***	***U.S.***	***Europe***	***Asia***	***Japan***	***Portugal***	***Asia excluding China***	***Asia + U.S. + Europe***	***World***
1990	3,218	5,744	9,092	9,861	1,116	60	6,642	24,697	33,937
1991	3,159	5,617	8,814	9,874	1,128	60	6,715	24,305	33,281
1992	3,307	5,683	8,783	10,238	1,140	64	6,932	24,703	33,295
1993	3,526	5,811	8,333	10,599	1,138	63	7,073	24,743	33,409
1994	3,692	5,901	7,897	11,001	1,195	65	7,309	24,799	33,629
1995	4,019	5,958	7,789	11,569	1,210	69	7,550	25,316	34,310
1996	4,117	6,121	7,809	11,892	1,226	67	7,775	25,822	34,980
1997	4,083	6,291	7,534	12,205	1,221	70	8,122	26,031	35,413
1998	4,171	6,281	7,526	12,195	1,184	74	8,024	26,002	35,684
1999	4,103	6,309	7,421	12,381	1,224	81	8,278	26,110	35,829
2000	4,371	6,487	7,463	12,915	1,239	81	8,544	26,865	36,680
2001	4,505	6,381	7,346	13,508	1,196	80	9,004	27,235	37,366
2002	4,835	6,312	7,347	14,111	1,229	84	9,276	27,769	38,123
2003	5,520	6,382	7,593	14,975	1,232	80	9,455	28,949	39,449
2004	6,289	6,496	7,459	16,097	1,231	81	9,809	30,053	40,841
2005	6,974	6,480	7,439	17,036	1,237	85	10,062	30,956	42,001
2006	7,692	6,364	7,415	18,359	1,185	78	10,667	32,137	42,779
2007	8,185	6,474	7,294	19,221	1,219	78	11,036	32,989	43,916
2008	8,455	6,289	7,343	19,701	1,130	73	11,246	33,333	44,372
2009	8,940	5,901	6,721	20,477	1,068	73	11,537	33,099	44,003
2010	9,473	6,147	6,931	21,377	1,114	67	11,904	34,455	45,748
2011	10,304	6,024	6,906	22,558	1,165	67	12,254	35,489	46,906
2012	10,684	5,823	6,929	23,297	1,207	68	12,613	36,049	47,599

Table 83 – Global GHGs Emissions by Gas.

World Resources Institute [5]

	MT CO_2 Equivalent			
Year	***Total CO2 (including LUCF)***	***Total CH4 (including LUCF)***	***Total N2O (including LUCF)***	***Total F-gas (excluding LUCF)***
1990	25,026	6,104	2,546	262
1991	24,383	6,093	2,537	268
1992	24,386	6,093	2,543	274
1993	24,522	6,073	2,534	279
1994	24,704	6,087	2,554	285
1995	25,330	6,091	2,598	291
1996	25,941	6,108	2,613	318
1997	26,256	6,196	2,615	346
1998	26,384	6,275	2,652	374
1999	26,502	6,281	2,645	401
2000	27,382	6,265	2,604	429
2001	28,001	6,291	2,611	463
2002	28,524	6,424	2,679	497
2003	29,701	6,515	2,704	530
2004	30,925	6,617	2,735	564
2005	31,928	6,715	2,760	598
2006	32,542	6,810	2,814	613
2007	33,494	6,911	2,883	628
2008	33,799	6,992	2,939	643
2009	33,319	7,045	2,981	657
2010	34,901	7,169	3,005	672
2011	35,924	7,212	3,047	723
2012	36,422	7,299	3,105	773

Table 84 – CH_4 Emission from domestic WWTPs, of Selected Countries.

UNFCCC [11][12]

	CH_4 (kt)			
Year	***U.S.***	***EU-28***	***Japan***	***Portugal***
1990	421	890.2	107.9	50.3
2005	401	526.5	74.6	40.8
2009	392	475.8	68.5	35.9
2010	384	468.2	67.3	35.8
2011	375	453.6	66.1	35.5
2012	373	436.7	64.8	35.4
2013	368	438.9	64.0	35.2

Table 85 – Global GHGs Emissions by Sector.

World Resources Institute [5]

	MT CO_2 Equivalent					
Year	***Energy***	***Industrial Processes***	***Agriculture***	***Waste***	***Land-Use Change and Forestry***	***Bunker Fuels***
1990	23,589	1,126	4,561	1,148	3,513	620
1991	23,799	1,146	4,540	1,164	2,632	628
1992	23,690	1,173	4,544	1,179	2,708	665
1993	23,773	1,212	4,513	1,195	2,716	661
1994	23,890	1,254	4,545	1,211	2,729	686
1995	24,441	1,300	4,592	1,226	2,751	710
1996	25,047	1,337	4,602	1,241	2,753	729
1997	25,293	1,374	4,586	1,255	2,905	756
1998	25,422	1,389	4,620	1,270	2,984	779
1999	25,585	1,433	4,668	1,285	2,858	815
2000	26,451	1,481	4,656	1,299	2,793	840
2001	26,706	1,552	4,683	1,315	3,109	808
2002	27,146	1,639	4,736	1,331	3,271	845
2003	28,286	1,758	4,761	1,347	3,297	852
2004	29,527	1,870	4,848	1,363	3,234	934
2005	30,515	1,982	4,906	1,379	3,219	985
2006	31,388	2,126	4,978	1,397	2,889	1,036
2007	32,407	2,234	5,078	1,416	2,781	1,079
2008	32,673	2,265	5,153	1,434	2,847	1,087
2009	32,203	2,370	5,211	1,453	2,766	1,043
2010	33,754	2,503	5,240	1,471	2,780	1,111
2011	34,655	2,723	5,330	1,483	2,715	1,133
2012	35,099	2,840	5,382	1,495	2,783	1,080

Table 86 – N_2O Emission from domestic WWTPs, of Selected Countries.

UNFCCC [11][12]

	N_2O (kt)			
Year	***U.S.***	***EU-28***	***Japan***	***Portugal***
1990	11	27.7	3.64	1.16
2005	15	26.2	3.67	1.36
2009	16	26.1	3.59	1.45
2010	16	26.4	3.55	1.45
2011	16	25.9	3.52	1.41
2012	16	25.8	3.40	1.37
2013	17	25.8	3.42	1.36

8.2 Appendix II

Table 87 – Molecular Weights [Aspen Plus].

T (ºC)	P (bar)	N_2O (g mol^{-1})	N_2 (g mol^{-1})	O2 (g mol^{-1})	CO_2 (g mol^{-1})	H_2O (g mol^{-1})	C_2H_6O (g mol^{-1})
25	1.01	44.013	28.013	31.998	44.009	18.015	62.068

Pure component scalar parameters

Parameters	Units	Data set	Component N2O	Component N2-02	Component O2	Component CO2	Component C2H6O-01	Component H2O
MW		1	44,01288000	28,01348000	31,99880000	44,00980000	62,06844000	18,01528000

Table 88 – Mass densities [Aspen Plus].

T (ºC)	P (bar)	N_2O (g)		N_2 (g)		O_2 (g)		CO_2 (g)	
25	1.01	0.0408	mol L^{-1}	0.0408	mol L^{-1}	0.0408	mol L^{-1}	0.0408	mol L^{-1}
		1.799	kg m^{-3}	1.145	kg m^{-3}	1.308	kg m^{-3}	1.798	kg m^{-3}

Pure component properties analysis results

TEMP	PRES	VAPOR RHO N2O	VAPOR RHO N2-02	VAPOR RHO O2	VAPOR RHO CO2
C	bar	mol/l	mol/l	mol/l	mol/l
25	1,01325	0,0408747	0,0408747	0,0408747	0,0408747

T (ºC)	P (bar)	H_2O (liquid)	
22	1.01	55.274	mol L^{-1}
		995.77	kg m^{-3}

Pure component properties analysis results

TEMP	PRES	LIQUID RHO H2O
C	bar	mol/l
22	1,01325	55,27375

T (ºC)	P (bar)	N_2 (g)		O_2 (g)	
25	2	0.081	mol L^{-1}	0.081	mol L^{-1}
		2.28	kg m^{-3}	2.60	kg m^{-3}

Pure component properties analysis results

TEMP	PRES	VAPOR RHO N2-02	VAPOR RHO O2
C	bar	mol/l	mol/l
25	2,01325	0,0812148	0,0812148

T (ºC)	P (bar)	N_2O (g)		N_2 (g)		O_2 (g)		CO_2 (g)	
13,4	44	1.847	mol L^{-1}	1.847	mol L^{-1}	1.847	mol L^{-1}	1.847	mol L^{-1}
		81.3	kg m^{-3}	51.8	kg m^{-3}	59.1	kg m^{-3}	81.285	kg m^{-3}
T (ºC)	P (bar)	N_2O (g)		N_2 (g)		O_2 (g)		CO_2 (g)	
-14	44	2.043	mol L^{-1}	2.043	mol L^{-1}	2.043	mol L^{-1}	2.043	mol L^{-1}
		89.9	kg m^{-3}	57.2	kg m^{-3}	65.4	kg m^{-3}	89.91	kg m^{-3}
T (ºC)	P (bar)	N_2O (liquid)		N_2 (liquid)		O_2 (liquid)		CO_2 (liquid)	
-14	44	22.063	mol L^{-1}	11.216	mol L^{-1}	13.604	mol L^{-1}	22.771	mol L^{-1}
		971.0	kg m^{-3}	314.2	kg m^{-3}	435.3	kg m^{-3}	1002.13	kg m^{-3}

Pure component properties analysis results

TEMP	PRES	VAPOR RHO N2O	VAPOR RHO N2-02	VAPOR RHO CO2	VAPOR RHO O2
C	bar	mol/l	mol/l	mol/l	mol/l
13,4	44,01325	1,847378	1,847378	1,847378	1,847378

Pure component properties analysis results

TEMP	PRES	VAPOR RHO N2O	VAPOR RHO N2-02	VAPOR RHO CO2	VAPOR RHO O2
C	bar	mol/l	mol/l	mol/l	mol/l
-14	44,01325	2,042702	2,042702	2,042702	2,042702

Pure component properties analysis results

TEMP	PRES	LIQUID RHO N2O	LIQUID RHO N2-02	LIQUID RHO CO2	LIQUID RHO O2
C	bar	mol/l	mol/l	mol/l	mol/l
-14	44,01325	22,06273	11,21671	22,77052	13,60455

T (ºC)	P (bar)	Ethylene glycol (liquid)	
-20	1.01	18.386	mol L^{-1}
		1141.2	kg m^{-3}

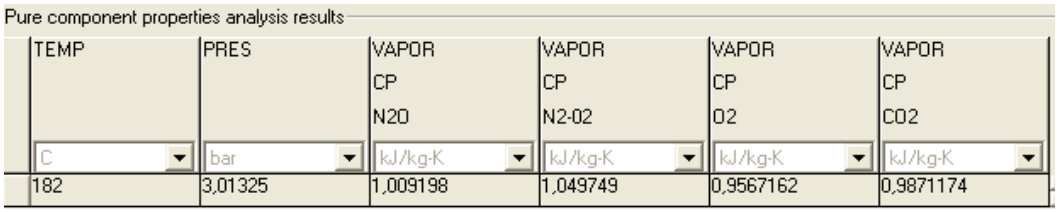
Pure component properties analysis results

TEMP	PRES	LIQUID RHO C2H6O-01
C	bar	mol/l
-20	1,01325	18,38603

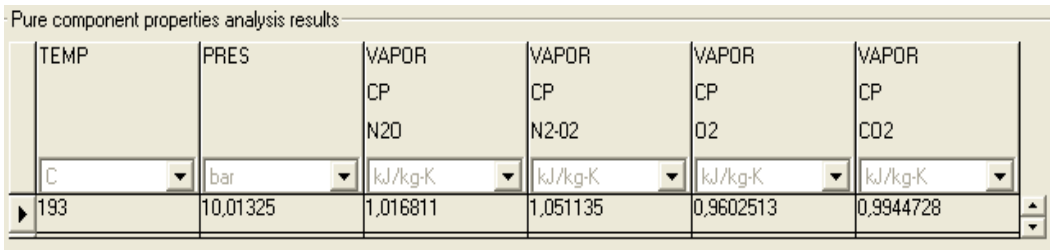
To convert mol to kg, it is used the molecular weights (Appendix II, Table 87) of each gas compound, respectively.

Table 89 – Specific Heats [Aspen Plus].

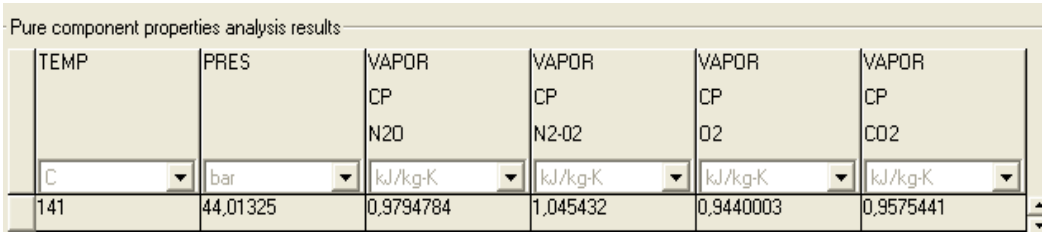
T (ºC)	P (bar)	N_2O (g)	N_2 (g)	O_2 (g)	CO_2 (g)
182	3	1.01 kJ kg^{-1} $ºC^{-1}$	1.05 kJ kg^{-1} $ºC^{-1}$	0.96 kJ kg^{-1} $ºC^{-1}$	0.98 kJ kg^{-1} $ºC^{-1}$
193	10	1.02 kJ kg^{-1} $ºC^{-1}$	1.05 kJ kg^{-1} $ºC^{-1}$	0.96 kJ kg^{-1} $ºC^{-1}$	0.99 kJ kg^{-1} $ºC^{-1}$
141	44	0.97 kJ kg^{-1} $ºC^{-1}$	1.04 kJ kg^{-1} $ºC^{-1}$	0.94 kJ kg^{-1} $ºC^{-1}$	0.96 kJ kg^{-1} $ºC^{-1}$


Pure component properties analysis results

TEMP	PRES	VAPOR CP N2O	VAPOR CP N2-O2	VAPOR CP O2	VAPOR CP CO2
C	bar	kJ/kg-K	kJ/kg-K	kJ/kg-K	kJ/kg-K
182	3,01325	1,009198	1,049749	0,9567162	0,9871174

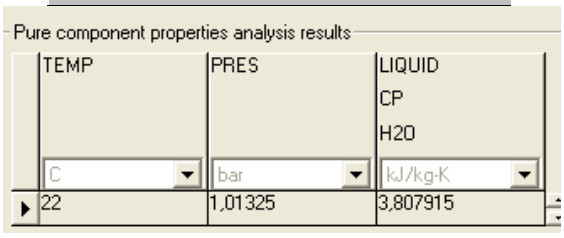

Pure component properties analysis results

TEMP	PRES	VAPOR CP N2O	VAPOR CP N2-O2	VAPOR CP O2	VAPOR CP CO2
C	bar	kJ/kg-K	kJ/kg-K	kJ/kg-K	kJ/kg-K
193	10,01325	1,016811	1,051135	0,9602513	0,9944728


Pure component properties analysis results

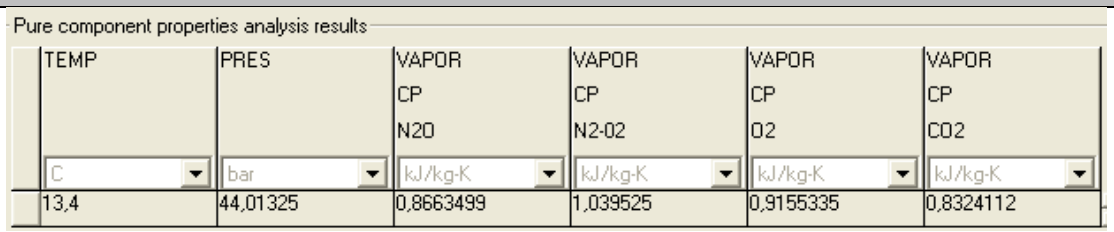
TEMP	PRES	VAPOR CP N2O	VAPOR CP N2-O2	VAPOR CP O2	VAPOR CP CO2
C	bar	kJ/kg-K	kJ/kg-K	kJ/kg-K	kJ/kg-K
141	44,01325	0,9794784	1,045432	0,9440003	0,9575441

T (ºC)	P (bar)	H_2O (liquid)
22	1.01	3.81 kJ kg^{-1} $ºC^{-1}$


Pure component properties analysis results

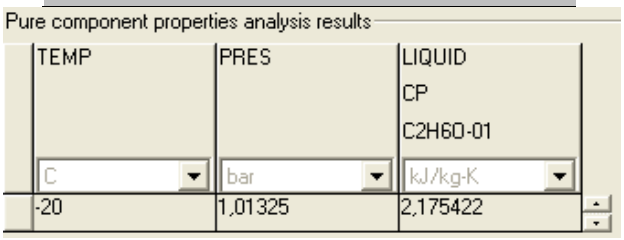
TEMP	PRES	LIQUID CP H2O
C	bar	kJ/kg-K
22	1,01325	3,807915

T (ºC)	P (bar)	N_2O (g)	N_2 (g)	O_2 (g)	CO_2 (g)
13.4	44	0.866 kJ kg^{-1} $ºC^{-1}$	1.039 kJ kg^{-1} $ºC^{-1}$	0.9155 kJ kg^{-1} $ºC^{-1}$	0.832 kJ kg^{-1} $ºC^{-1}$


Pure component properties analysis results

TEMP	PRES	VAPOR CP N2O	VAPOR CP N2-O2	VAPOR CP O2	VAPOR CP CO2
C	bar	kJ/kg-K	kJ/kg-K	kJ/kg-K	kJ/kg-K
13,4	44,01325	0,8663499	1,039525	0,9155335	0,8324112

T (ºC)	P (bar)	Ethylene glycol (liquid)
-20	1.01	2.175 kJ kg^{-1} $ºC^{-1}$



8.3 Appendix III

Exchange rate (Jan. 20, 2016): 1 US $ = 0.915 €

Case Scenario 1	VP – 101 A/B/C/D	VP – 102 A/B/C/D
Power of 1 pump: **P (W)**	995.4	490.1
Quantity	4	4
Total Power (W)	**3,981.7**	**1,960.3**
Inlet flow rate (m^3/h)	168	82.21
Inlet flow rate (m^3/min)	2.8	1.4
Inlet flow rate (cfm)	99	48

References for prices (scenario 1):

Membrane vessels [99], Membrane rolls [100], Vacuum pumps [101], 2-way Flanged and Manual valves [102]**,** 3-way Flanged valves [103], Flow control valves [104].

Case Scenario 2	D-101	HE-101	C-101
V (m^3)	5	-	-
V (gallon)	1,321	-	-
Heat transf. A (m^2)	-	59.7	-
Heat transf. A (ft^2)	-	643	-
P (kW)	-	-	361.56
P (horsepower)	-	-	485

References for prices (scenario 2):

Compressor, Heat exchanger, Drum, Pumps [105], Membrane vessels [99], Membrane rolls [100], 2-way Flanged and Manual valves [102] [106], 3-way Flanged valves [103] [107], Flow control, Check and Relief valves [104] [108], Steam trap valve [109], Air vent valve [110].

Case Scenario 3	D-101	HE-101	HE-102	C-101	C-102
V (m^3)	5	-	-	-	-
V (gallon)	1,321	-	-	-	-
Heat transf. A (m^2)	-	49.2	71.2	-	-
Heat transf. A (ft^2)	-	530	766	-	-
P (kW)	-	-	-	1,114	698
P (horsepower)	-	-	-	1,494	936

References for prices (scenario 3):

Compressor, Heat exchangers, Drums, Pumps, Adsorption columns, Buffer tank, Liquefier, Storage tanks [105], Membrane vessels [99], Membrane rolls [100], 2-way Flanged and Manual valves [102] [106], 3-way Flanged valves [103] [107], Flow control, Check and Relief valves [104] [108], Steam trap valve [109] [111], Air vent valve [110], Adsorbent GAC ($/ton) [112].

Table 90 – Base Equipment Cost, in each case scenario.

Case Scenario 1

Base Equipment	Quantity	Type	Max. Operating P	Material	2014 Cost ($/unit)	2016 Cost ($/unit)	2016 Total ($)	2016 Total (€)
Membrane Vessel, MB-101; 102	8	model 40E30N (4''x40'')	20 bar	Ethylene Propylene	-	$ 170	$ 1,360	1,245 €
Membrane Roll, MB-101, 102	8	model: C080A330R	-	Cellulose Acetate	-	$ 420	$ 3,357	3,073 €
Vaccum Pump, VP-101	4	145 CFM free air (Battioni & Pagani MEC 4000)	2 bar	-	-	$ 1,660	$ 13,278	12,154 €
Vaccum Pump, VP-102	4							
2-Way Flanged Valve (1.5'')	**61**	class 150	19 bar	Carbon Steel	$ 302	$ 302	$ 18,412	16,853 €
3-Way Flanged Valve (1.5'')	**6**	class 150	19 bar	Carbon Steel	$ 1,064	$ 1,065	$ 6,390	5,849 €
Flow Control Valve (1.5'')	**17**	class 150	19 bar	-	$ 2,110	$ 2,112	$ 35,909	32,870 €
Manual Valve (1.5'')	**17**	class 150	19 bar	Carbon Steel	$ 302	$ 302	$ 5,131	4,697 €
						TOTAL	**$ 83,837**	**76,740 €**

Case Scenario 2

Base Equipment	Quantity	Type	Max. Operating P	Material	2014 Cost ($/unit)	2016 Cost ($/unit)	2016 Total ($)	2016 Total (€)
Compressor, C-101	1	centrifugal	7 bar/ 125 psi	Carbon Steel	$ 155,600	$ 155,771	$ 155,771	142,585 €
Heat Exchanger, H-101	1	shell/tube, fixed	10 bar/150 psi	Carbon Steel	$ 34,600	$ 34,638	$ 34,638	31,706 €
Drum, D-101	1	horiz tank, round ends	atmospheric	Carbon Steel	$ 8,600	$ 8,609	$ 8,609	7,881 €
Membrane Vessel, MB-101; 102	2	model 40E30N (4''x40'')	20 bar	Ethylene Propylene	-	$ 170	$ 340	311 €
Membrane Roll, MB-102	1	model: C020A330R	-	Cellulose Acetate	-	$ 261	$ 680	623 €
Membrane Roll, MB-101	1	model: C080A330R	-			$ 420		
Pump, P-101 A/B (3'')	4	centrifugal, horiz. threared w/ motor	-	Cast Iron	$ 2,300	$ 2,303	$ 9,210	8,430 €
Pump, P-102 A/B (3'')			-					
2-Way Flanged Valve (1.5'')	21	class 150	19 bar	Carbon Steel	$ 302	$ 302	$ 6,338	5,802 €
2-Way Flanged Valve (3/4'')	2	class 150	19 bar		$ 142	$ 142	$ 285	261 €
2-Way Flanged Valve (3'')	7	class 150	19 bar		$ 827	$ 828	$ 5,796	5,305 €
3-Way Flanged Valve (1.5'')	1	class 150	19 bar	Carbon Steel	$ 1,064	$ 1,065	$ 1,065	975 €
3-Way Flanged Valve (3'')	4	class 150	19 bar		$ 2,038	$ 2,040	$ 8,159	7,469 €
Flow Control Valve (1.5'')	5	class 150	19 bar	-	$ 2,110	$ 2,112	$ 10,562	9,668 €
Flow Control Valve (3'')	2	class 150	19 bar		$ 3,153	$ 3,156	$ 6,313	5,779 €
Manual Valve (1.5'')	5	class 150	19 bar	Carbon Steel	$ 302	$ 302	$ 1,509	1,381 €
Manual Valve (3'')	3	class 150	19 bar		$ 827	$ 828	$ 2,484	2,274 €
Check Valve (3'')	4	class 125	14 bar	-	$ 1,715	$ 1,717	$ 6,868	6,286 €
Relief Valve (1.5'')	1	class 150	19 bar	-	$ 1,559	$ 1,561	$ 1,561	1,429 €
Steam Trap Valve (3/4'')	1	Float & Thermostatic	14 bar	Cast Iron	-	$ 569	$ 569	521 €
Air Vent Valve (3/4'')	1	Gorton #1	atmospheric	-	-	$ 65	$ 65	59 €
						TOTAL	**$ 260,822**	**238,743 €**

Case Scenario 3

Base Equipment	Quantity	Type	Max. Operating P	Material	2016 Cost ($/ton)	2014 Cost ($/unit)	2016 Cost ($/unit)	2016 Total ($)	2016 Total (€)
Compressor, C-101	1	centrifugal	68 bar	Carbon Steel	-	$ 686,100	$ 686,855	$ 686,855	628,711 €
Compressor, C-102	1		68 bar		-	$ 472,000	$ 472,519	$ 472,519	432,520 €
Heat Exchanger, H-101	1	shell/tube, fixed, U	10.4 bar	Carbon Steel	-	$ 29,400	$ 29,432	$ 29,432	26,941 €
Heat Exchanger, H-102	1	medium	62.1 bar		-	$ 70,300	$ 70,377	$ 70,377	64,420 €
Drum, D-101	1	horiz. tank, round ends	atmospheric	Carbon Steel	-	$ 8,600	$ 8,609	$ 8,609	7,881 €
Membrane Vessel, MB-101; 102	2	model 40E100 (4''x40'')	68 bar	Ethylene Propylene	-	-	$ 475	$ 950	870 €
Membrane Roll, MB-101; 102	2	model C020A330R	-	Cellulose Acetate	-	-	$ 261	$ 521	477 €
Pump, P-101 A/B, P-103 A/B (3'')	4	centrifugal, horiz.	-	Cast Iron	-	$ 2,300	$ 2,303	$ 9,210	8,430 €
Pump, P-102 A/B (2'')	2	threared w/ motor	-		-	$ 1,400	$ 1,402	$ 2,803	2,566 €
Adsorption Column	2	Vessel: Column, No Internals, Medium	-	Carbon Steel	-	$ 32,100	$ 32,135	$ 64,271	58,830 €
Adsorbent	2x (1.5 ton)	Granular	-	Activated Carbon	$ 1,325	-	-	$ 3,975	3,639 €
Buffer Tank	1	vert. tank, cone top & bottom, small	-	Carbon Steel	-	$ 9,200	$ 9,210	$ 9,210	8,430 €
Liquefier	1	condenser, small	62.1 bar	Carbon Steel	-	$ 19,100	$ 19,121	$ 19,121	17,502 €
Storage Tank	2	vert. tank, cone top & bottom, small	-	Carbon Steel	-	$ 13,300	$ 13,315	$ 26,629	24,375 €
2-Way Flanged Valve (1.5'')	30	class 150	19 bar	Carbon Steel	-	$ 302	$ 302	$ 9,055	8,288 €
2-Way Flanged Valve (1.5'')	57	class 300	48 bar		-	$ 419	$ 420	$ 23,932	21,906 €
2-Way Flanged Valve (3/4'')	2	class 150	19 bar		-	$ 142	$ 142	$ 285	261 €
2-Way Flanged Valve (3/4'')	2	class 300	48 bar		-	$ 185	$ 186	$ 371	340 €
2-Way Flanged Valve (2'')	4	class 150	19 bar		-	$ 403	$ 404	$ 1,615	1,478 €
2-Way Flanged Valve (3'')	7	class 150	19 bar		-	$ 827	$ 828	$ 5,796	5,305 €
3-Way Flanged Valve (1.5'')	1	class 150	19 bar	Carbon Steel	-	$ 1,064	$ 1,065	$ 1,065	975 €
3-Way Flanged Valve (1.5'')	6	class 300	48 bar		-	$ 1,299	$ 1,300	$ 7,801	7,140 €
3-Way Flanged Valve (2'')	2	class 150	19 bar		-	$ 1,123	$ 1,124	$ 2,249	2,059 €
3-Way Flanged Valve (3'')	4	class 150	19 bar		-	$ 2,038	$ 2,040	$ 8,159	7,469 €
Flow Control Valve (1.5'')	7	class 150	19 bar	-	-	$ 2,110	$ 2,112	$ 14,786	13,535 €
Flow Control Valve (2'')	16	class 300	48 bar		-	$ 2,232	$ 2,234	$ 35,751	32,725 €
Flow Control Valve (2'')	1	class 150	19 bar		-	$ 2,176	$ 2,178	$ 2,178	1,994 €
Flow Control Valve (3'')	2	class 150	19 bar		-	$ 3,153	$ 3,156	$ 6,313	5,779 €
Manual Valve (1.5'')	7	class 150	19 bar	Carbon Steel	-	$ 302	$ 302	$ 2,113	1,934 €
Manual Valve (1.5'')	19	class 300	48 bar		-	$ 419	$ 420	$ 7,977	7,302 €
Manual Valve (2'')	1	class 150	19 bar		-	$ 403	$ 404	$ 404	369 €
Manual Valve (3'')	3	class 150	19 bar		-	$ 827	$ 828	$ 2,484	2,274 €
Check Valve (2'')	2	class 125	14 bar	-	-	$ 1,505	$ 1,507	$ 3,013	2,758 €
Check Valve (3'')	4	class 125	14 bar		-	$ 1,715	$ 1,717	$ 6,868	6,286 €
Relief Valve (1.5'')	1	class 150	19 bar	-	-	$ 1,559	$ 1,561	$ 1,561	1,429 €
Relief Valve (1.5'')	1	class 300	48 bar		-	$ 1,608	$ 1,610	$ 1,610	1,473 €
Steam Trap Valve (3/4'')	1	Float & Thermostatic	14 bar	Cast Iron	-	-	$ 569	$ 569	521 €
Steam Trap Valve (3/4'')	1	Thermostatic Radiator	62 bar	Alloy Steel	-	-	$ 1,628	$ 1,628	1,490 €
Steam Trap Valve (1.5'')	1	Inverted Bucket	48 bar	Forged Steel	-	-	$ 6,913	$ 6,913	6,327 €
Air Vent Valve (3/4'')	1	Gorton #1	atmospheric	-	-	-	$ 65	$ 65	59 €
							TOTAL	$ 1,559,043	1,427,068 €

Activated Carbon: 1,500 kg = 3,307 pounds (**adsorber vessels** weight)

8.4 Appendix IV

Table 91 – Break-even Point, in case of scenario 1.

	1	2	3	4	5	6	7	8	9	10
BEP (value, €)	***2018***	***2019***	***2020***	***2021***	***2022***	***2023***	***2024***	***2025***	***2026***	***2027***
Fixed Costs	28,549 €	28,549 €	28,549 €	28,549 €	28,549 €	28,549 €	28,549 €	28,549 €	28,549 €	28,549 €
Variable Costs	33,732 €	33,732 €	33,732 €	36,805 €	33,732 €	33,732 €	33,732 €	36,805 €	33,732 €	33,732 €
N2O (ton)	1,209	1,209	1,209	1,209	1,209	1,209	1,209	1,209	1,209	1,209
Unit Variable Costs (€/ton)	28 €	28 €	28 €	30 €	28 €	28 €	28 €	30 €	28 €	28 €
Annual Income	**279,038 €**	**279,038 €**	**279,038 €**	**279,038 €**	**279,038 €**	**279,038 €**	**279,038 €**	**279,038 €**	**279,038 €**	**279,038 €**
(€/ton)	231 €	231 €	231 €	231 €	231 €	231 €	231 €	231 €	231 €	231 €

	0	1	2	3	4	5	6	7	8	9	10
BEP (quantity, ton)		***2018***	***2019***	***2020***	***2021***	***2022***	***2023***	***2024***	***2025***	***2026***	***2027***
N2O Production (ton)	0	121	242	363	484	604	725	846	967	1,088	1,209
Fixed Costs	28,549 €	28,549 €	28,549 €	28,549 €	28,549 €	28,549 €	28,549 €	28,549 €	28,549 €	28,549 €	28,549 €
Variable Costs		3,373 €	6,746 €	10,120 €	14,722 €	16,866 €	20,239 €	23,612 €	29,444 €	30,359 €	33,732 €
Total Costs	28,549 €	31,922 €	35,295 €	38,668 €	43,271 €	45,415 €	48,788 €	52,161 €	57,992 €	58,908 €	62,281 €
Revenues	**- €**	**27,904 €**	**55,808 €**	**83,711 €**	**111,615 €**	**139,519 €**	**167,423 €**	**195,326 €**	**223,230 €**	**251,134 €**	**279,038 €**

Table 92 – Break-even Point, in case of scenario 2.

	1	2	3	4	5	6	7	8	9	10
BEP (value, €)	***2018***	***2019***	***2020***	***2021***	***2022***	***2023***	***2024***	***2025***	***2026***	***2027***
Fixed Costs	59,406 €	59,406 €	59,406 €	59,406 €	59,406 €	59,406 €	59,406 €	59,406 €	59,406 €	59,406 €
Variable Costs	374,804 €	374,804 €	374,804 €	375,427 €	374,804 €	374,804 €	374,804 €	375,427 €	374,804 €	374,804 €
N2O (ton)	1,209	1,209	1,209	1,209	1,209	1,209	1,209	1,209	1,209	1,209
Unit Variable Costs (€/ton)	310 €	310 €	310 €	311 €	310 €	310 €	310 €	311 €	310 €	310 €
Annual Incomes	**279,038 €**	**279,038 €**	**279,038 €**	**279,038 €**	**279,038 €**	**279,038 €**	**279,038 €**	**279,038 €**	**279,038 €**	**279,038 €**
(€/ton)	231 €	231 €	231 €	231 €	231 €	231 €	231 €	231 €	231 €	231 €

	0	1	2	3	4	5	6	7	8	9	10
BEP (quantity, ton)		***2018***	***2019***	***2020***	***2021***	***2022***	***2023***	***2024***	***2025***	***2026***	***2027***
N2O Production (ton)	0	121	242	363	484	604	725	846	967	1,088	1,209
Fixed Costs	59,406 €	59,406 €	59,406 €	59,406 €	59,406 €	59,406 €	59,406 €	59,406 €	59,406 €	59,406 €	59,406 €
Variable Costs	- €	37,480 €	74,961 €	112,441 €	150,171 €	187,402 €	224,883 €	262,363 €	300,342 €	337,324 €	374,804 €
Total Costs	59,406 €	96,886 €	134,367 €	171,847 €	209,577 €	246,808 €	284,288 €	321,769 €	359,747 €	396,730 €	434,210 €
Revenues	**- €**	**27,904 €**	**55,808 €**	**83,711 €**	**111,615 €**	**139,519 €**	**167,423 €**	**195,326 €**	**223,230 €**	**251,134 €**	**279,038 €**

Table 93 – Break-even Point, in case of scenario 3.

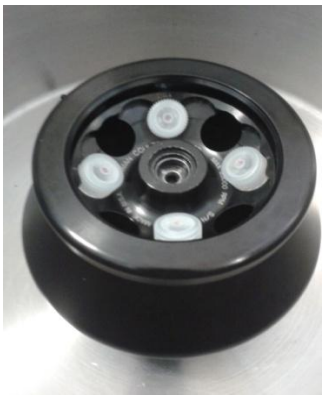
	1	2	3	4	5	6	7	8	9	10
BEP (value, €)	*2018*	*2019*	*2020*	*2021*	*2022*	*2023*	*2024*	*2025*	*2026*	*2027*
Fixed Costs	296,621 €	296,621 €	296,621 €	296,621 €	296,621 €	296,621 €	296,621 €	296,621 €	296,621 €	296,621 €
Variable Costs	2,110,810 €	2,114,448 €	2,114,448 €	2,114,926 €	2,114,448 €	2,114,448 €	2,114,448 €	2,114,926 €	2,114,448 €	2,114,448 €
N2O (ton)	686	686	686	686	686	686	686	686	686	686
Unit Variable Costs (€/ton)	3,075 €	3,080 €	3,080 €	3,081 €	3,080 €	3,080 €	3,080 €	3,081 €	3,080 €	3,080 €
Annual Income	**2,745,718 €**	**2,745,718 €**	**2,745,718 €**	**2,745,718 €**	**2,745,718 €**	**2,745,718 €**	**2,745,718 €**	**2,745,718 €**	**2,745,718 €**	**2,745,718 €**
(€/ton)	4,000 €	4,000 €	4,000 €	4,000 €	4,000 €	4,000 €	4,000 €	4,000 €	4,000 €	4,000 €

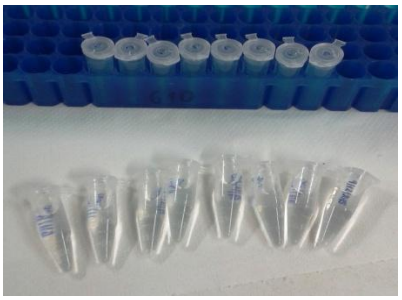
	0	1	2	3	4	5	6	7	8	9	10
BEP (quantity, ton)		*2018*	*2019*	*2020*	*2021*	*2022*	*2023*	*2024*	*2025*	*2026*	*2027*
N2O Production (ton)	0	69	137	206	275	343	412	481	549	618	686
Fixed Costs	296,621 €	296,621 €	296,621 €	296,621 €	296,621 €	296,621 €	296,621 €	296,621 €	296,621 €	296,621 €	296,621 €
Variable Costs		211,081 €	422,890 €	634,335 €	845,970 €	1,057,224 €	1,268,669 €	1,480,114 €	1,691,941 €	1,903,004 €	2,114,448 €
Total Costs	296,621 €	507,702 €	719,511 €	930,956 €	1,142,591 €	1,353,845 €	1,565,290 €	1,776,735 €	1,988,562 €	2,199,625 €	2,411,069 €
Revenues	**- €**	**274,572 €**	**549,144 €**	**823,715 €**	**1,098,287 €**	**1,372,859 €**	**1,647,431 €**	**1,922,002 €**	**2,196,574 €**	**2,471,146 €**	**2,745,718 €**

In each case scenario, **fixed costs** account for CAPEX amortization, financial charges, salaries and also maintenance, and **variable costs** account for total OPEX.

8.5 Appendix V: N_2O Monitoring

During the present study, it was also possible to participate in a N_2O campaign, related with FCT/UNL investigation studies. This campaign consisted in a weekly sampling of the entrance and exit of the biological treatment, at Chelas's WWTP (Portugal). Then, samples had to be prepared and stored, in FCT/UNL laboratories. An approach to segmented flow analysis was also possible to take.





In 2015, the average of ammonia concentration of the plant's influent was 20 mg NH_4-N L^{-1} and the average of nitrate concentration of the plant's effluent was 0.32 mg NO_3-N L^{-1}. This values are much lower than $TKN_{influent}$ and $TN_{effluent}$ from Alcântara's WWTP (54 g N m^{-3} and 29 g N m^{-3}, respectively), since Chelas's WWTP has a lower influent flow rate. In 2015, the average of wastewater flow rate was 2,335 m^3 h^{-1} and 7,038 m^3 h^{-1} in Chela's WWTP and Alcântara's WWTP, respectively.

9. Attachments

9.1 Annex I

Notes

Theoretical maximum process efficiency was determined by the demand in oxygen and organic reducing power required to completely treat the average U.S. *per capita* nitrogen and BOD_L loads. The BOD that remains after nitrogen removal is recovered as biogas CH_4 and converted to energy with 100% conversion efficiency [2].

Assumptions

T=25ºC;
NH3 is the N-source for cell synthesis;
For partial nitrification, SRT = 6 days and f_s^0 = 0.14;
For complete nitrification, SRT = 10 days and f_s^0 = 0.11;
$\mathbf{f_s^0}$ of denitrification for CANON corresponds to Anammox;

$\mathbf{f_s^0}$ is defined as the maximum biomass yield expressed in dimensionless units (e.g. oxygen demand of biomass produced divided by the oxygen demand of the electron donor consumed), and calculated by the free energy protocol of Rittman and McCarty [2].

$\mathbf{f_s}$ is the observed yield expressed in dimensionless units and adjusted for decay:

$$f_s = f_s^0 \left(\frac{1 + 0.2bSRT}{1 + bSRT} \right)$$

[2]

b: specific decay rate (day^{-1})
SRT: solids residence time (day)

Analysis assumes energy recovery from soluble and particulate BOD, with complete conversion of organic nitrogen and free ammonia [2].

9.2 Annex II

Figure 53 – Process for Recovery and Purification of N_2O, with Wet Scrubbing. U.S. Patent 2014/0366576 A1 [44]

Production of 99.9% N_2O								
From	Feeding	Wet Scrubbing	Adsorption	Liquefier	Releaser	Releaser	Flash	Flash
To	Wet Scrubbing	Compressor	Liquefier	Releaser	Adsorption	Flash	2nd Stage compressor	Storage
Temperature (° C.)	20.0	25.3	−1.0	−49.0	−66.3	−39.7	−39.7	−39.7
Pressure (MPa)	0.15315	0.101325	3.041325	3.001325	1.101325	1.001325	1.001325	1.001325
Mass Flow (kg/hr)	164.2169	153.7882	168.4743	168.4743	101.3516	67.1206	17.25173	49.86887
Component Fraction by Volume								
O_2	0.038963	0.040383	0.038783	0.038783	0.057258	2.20E−03	7.76E−03	2.42E−04
N_2	0.418598	0.433863	0.412509	0.412509	0.615926	9.67E−03	0.035672	5.42E−04
N_2O	0.474245	0.490901	0.546589	0.546589	0.323656	0.988075	0.956375	0.999209
H_2O	9.99E−04	0.032358	6.85E−07	6.85E−07	6.76E−10	2.04E−06	1.19E−08	2.75E−06
CO	2.10E−03	2.17E−03	2.07E−03	2.07E−03	3.09E−03	4.56E−05	1.68E−04	2.46E−06
CO_2	0.065038	2.68E−04	5.07E−07	5.07E−07	3.05E−07	9.06E−07	9.15E−07	9.04E−07
NO	5.00E−05	5.18E−05	5.06E−05	5.06E−05	7.32E−05	5.98E−06	2.03E−05	9.44E−07
NO_2	9.99E−06	3.09E−08	2.85E−08	2.85E−08	8.59E−11	8.47E−08	1.59E−09	1.14E−07

Figure 54 – Process for Recovery and Purification of N_2O, without Wet Scrubbing. U.S. Patent 2014/0366576 A1 [44]

Production of 99.9% N_2O without Wet Scrubbing							
From	Feeding	Adsorption	Liquefier	Releaser	Releaser	Flash	Flash
To	Compressor	Liquefier	Releaser	Adsorption	Flash	2nd Stage compressor	Storage
Temperature (° C.)	20.0	−1.0	−49.0	−66.3	−39.6	−39.6	−39.6
Pressure (MPa)	0.15315	3.041325	3.001325	1.101325	1.001325	1.001325	1.001325
Mass Flow (kg/hr)	164.2169	169.5656	169.5656	101.4353	68.13675	18.19446	49.94228
Component Fraction by Volume							
O_2	0.038963	0.038587	0.038587	0.057228	2.20E−03	7.50E−03	2.34E−04
N_2	0.418598	0.410342	0.410342	0.615577	9.67E−03	0.034403	5.23E−04
N_2O	0.474245	0.548891	0.548891	0.323999	0.987945	0.957799	0.999088
H_2O	9.99E−04	9.72E−08	9.72E−08	9.53E−11	2.87E−07	1.70E−09	3.92E−07
CO	2.10E−03	2.06E−03	2.06E−03	3.09E−03	4.55E−05	1.62E−04	2.37E−06
CO_2	0.065038	6.33E−05	6.33E−05	3.79E−05	1.13E−04	1.14E−04	1.12E−04
NO	5.00E−05	5.04E−05	5.04E−05	7.31E−05	5.97E−06	1.97E−05	9.14E−07
NO_2	9.99E−06	9.77E−06	9.77E−06	2.93E−08	2.88E−05	5.51E−07	3.92E−05

9.3 Annex III

AIR LIQUIDE

ALPHAGAZ 1 N2O

N_2O

Enciclopédia dos Gases Air Liquide – Pag.s : 1053 – 1060

***ALPHAGAZ** é a solução simples para optimizar a cadeia analítica*

- **Aplicações**
  Gás para chama (AAS)

- **Informações de transporte**
  Gás liquefeito

Designação oficial	Protoxido de azoto
N°ONU	1070
ADR/RID	Classe 2 Código de classificação 2 O

- **Ficha de Segurança Produto**
  N° 093A-1
  Acesso : www.airliquide.pt

- **Propriedades físicas**

Peso molecular	44,01 g/mol
Densidade relativa, gás	1,5 (ar=1)
Densidade relativa, líquido	1,2 (água=1)
N° CAS	10024-97-2

- **Propriedades**
  Identificação de perigos: O gás líquido pode causar queimaduras por frio. Vermelhidão. Queimadura criogénica. Oxidante. Alimenta fortemente a combustão. Pode reagir violentamente com substâncias combustíveis
  Tipo de inflamabilidade: Não inflamável
  Protecção individual: nao fumar durante a manipulacao do producto. Verifique se existe ventlilação adequada. Proteja olhos, face e pele de derrames de liquido. Não use óleo ou massa lubrificante.

- **Equipamento das garrafas**
  Rosca da válvula:
  AFNOR G (26 x 1,5 SI - RH macho)
  Côr da ogiva: azul claro (RAL 5012)

- **Especificações do produto**

Pureza global (% mol) N_2O	Impurezas (ppm-mol)		Modo de fornecimento	Dimensão da embalagem	Pressão (bar)	Capacidade (kg)	Referência produto
≥ 99,6	N_2	≤ 0,4 % mol	Garrafa	L50	44	35	P0311L50R0A001

Prazo de validade: 60 meses

9.4 Annex IV

Figure 55 – Approximate Overall Heat Transfer Coefficients [55].

Hot Fluid	Cold Fluid	U W/m²-°C
Sensible Heat Transfer (No Change of Phase)		
Water	Water	850–1700
Organic solvents	Water	280–850
Gases	Water	20–280
Light oils	Water	340–900
Heavy oils	Water	60–280
Organic solvents	Light oil	110–400
Water	Brine	570–1140
Organic solvents	Brine	170–510
Gases	Brine	20–280
Organic solvents	Organic solvents	110–340
Heavy oils	Heavy oils	50–280
Heaters		
Steam	Water	1400–4300
Steam	Light oils	280–850
Steam	Heavy oils	60–450
Steam	Organic solvents	570–1140
Steam	Gases	30–280
Dowtherm	Gases	20–230
Dowtherm	Heavy oils	50–340
Flue gas	Aromatic HC and Steam	30–85
Evaporators		
Steam	Water	2000–4300
Steam	Light oils	450–1000
Steam	Heavy oils (vacuum)	140–430
Steam	Organic solvents	570–1140
Water	Refrigerants	430–850
Organic solvents	Refrigerants	170–570
Condensers		
Steam (pressure)	Water	2000–4300
Steam (vacuum)	Water	1700–3400
Saturated organic solvents near atmos.	Water	570–1140
Saturated organic solvents with some non-cond	Water, brine	280–680
Organic solvents, atmospheric and high non-condensable	Water, brine	280–680
Aromatic vapors, atmospheric with non-condensables	Water	30–170
Organic solvents, vacuum and high non-condensables	Water, brine	60–280
Low boiling hydrocarbon, atmospheric	Water	450–1140
High boiling hydrocarbon, vacuum	Water	60–170

9.5 Annex V

- **Assumptions**

Exchange rate (Jan. 20, 2016): 1 US $ = 0.915€

Operation time = 350 days (8400 h)

Natural gas prices for industrial consumers in Portugal, $C_{S,f}$ = 11.42 €/GJ (2015) **[113]**

Regeneration Air and Nitrogen Gas (P = 2 bar)**:**

$$a = \left(4.5 \times 10^{-5}\right) * q^{-0.3} * ln(p)$$

$$b = (9 \times 10^{-4}) * ln(p)$$

$$0.1 < q < 100\ m^3 s^{-1}$$

$$2 < p < 35\ bar$$

[90]

Ethylene Glycol (T = 253 K, -20ºC)**:**

$$a = 0.5 * {Q_c}^{-0.9} * T^{-3}$$

$$b = \left(1.1 \times 10^{6}\right) * T^{-5}$$

$$1 < Q_c < 1000\ kJ\ s^{-1}$$

$$0 < T < 300\ K$$

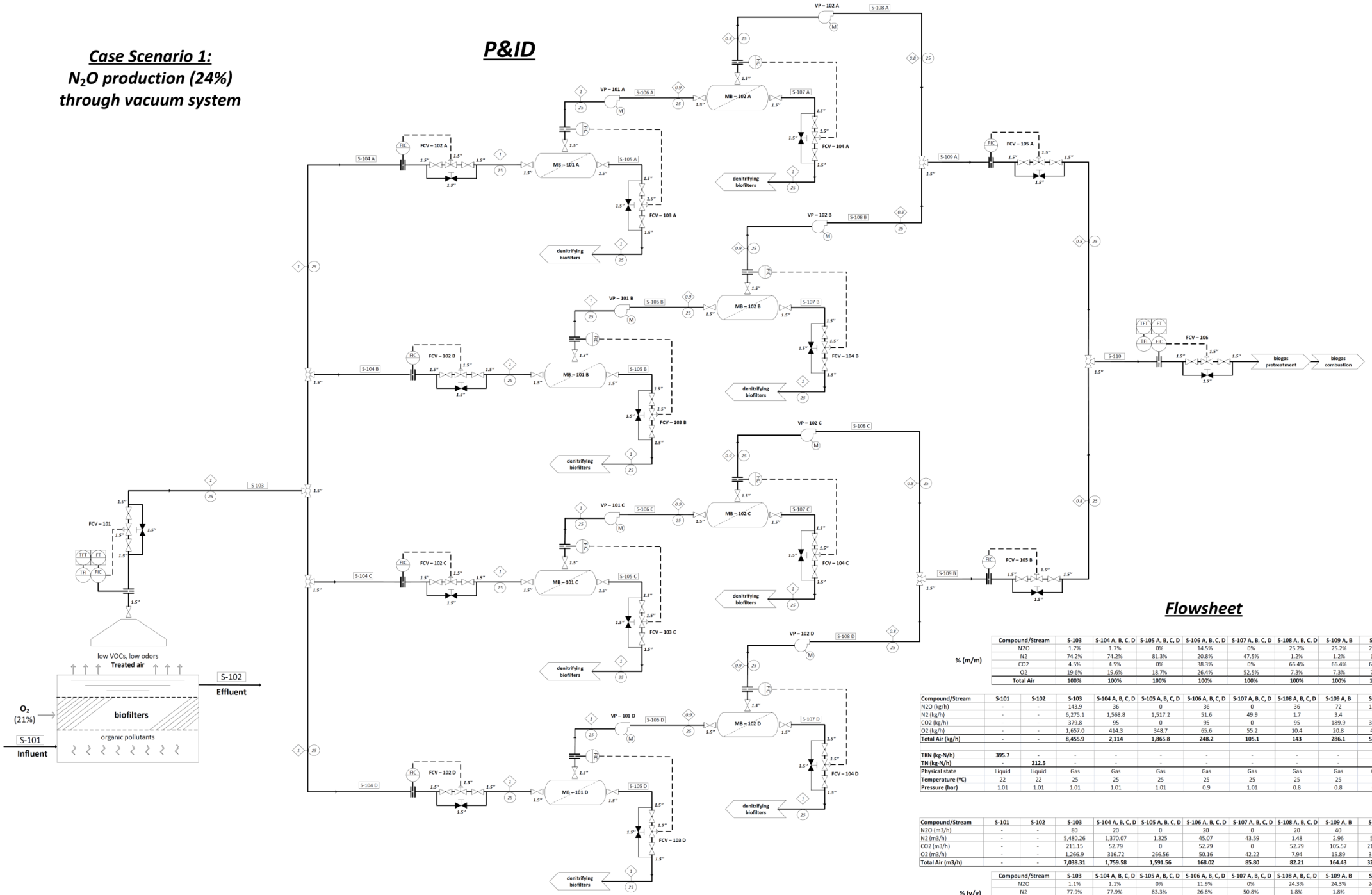
[90]

9.6 Annex VI

- **Flowsheet and P&ID Sections, for each case scenario:**

Case Scenario 1:
N_2O production (24%) through vacuum system

P&ID



Flowsheet

Compound/Stream	S-103	S-104 A, B, C, D	S-105 A, B, C, D	S-106 A, B, C, D	S-107 A, B, C, D	S-108 A, B, C, D	S-109 A, B	S-110
N2O	1.7%	1.7%	0%	14.5%	0%	25.2%	25.2%	25.2%
N2	74.2%	74.2%	81.3%	20.8%	47.5%	1.2%	1.2%	1.2%
CO2	4.5%	4.5%	0%	38.3%	0%	66.4%	66.4%	66.4%
O2	19.6%	19.6%	18.7%	26.4%	52.5%	7.3%	7.3%	7.3%
Total Air	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**

% (m/m)

Compound/Stream	S-101	S-102	S-103	S-104 A, B, C, D	S-105 A, B, C, D	S-106 A, B, C, D	S-107 A, B, C, D	S-108 A, B, C, D	S-109 A, B	S-110
N2O (kg/h)	-	-	143.9	36	0	36	0	36	72	143.9
N2 (kg/h)	-	-	6,275.1	1,568.8	1,517.2	51.6	49.9	1.7	3.4	6.8
CO2 (kg/h)	-	-	379.8	95	0	95	0	95	189.9	379.8
O2 (kg/h)	-	-	1,657.0	414.3	348.7	65.6	55.2	10.4	20.8	41.6
Total Air (kg/h)	**-**	**-**	**8,455.9**	**2,114**	**1,865.8**	**248.2**	**105.1**	**143**	**286.1**	**572.1**
TKN (kg-N/h)	**395.7**	-	-	-	-	-	-	-	-	-
TN (kg-N/h)		**212.5**	-	-	-	-	-	-	-	-
Physical state	Liquid	Liquid	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Gas
Temperature (ºC)	22	22	25	25	25	25	25	25	25	25
Pressure (bar)	1.01	1.01	1.01	1.01	1.01	0.9	1.01	0.8	0.8	0.8

Compound/Stream	S-101	S-102	S-103	S-104 A, B, C, D	S-105 A, B, C, D	S-106 A, B, C, D	S-107 A, B, C, D	S-108 A, B, C, D	S-109 A, B	S-110
N2O (m3/h)	-	-	80	20	0	20	0	20	40	80
N2 (m3/h)	-	-	5,480.26	1,370.07	1,325	45.07	43.59	1.48	2.96	5.93
CO2 (m3/h)	-	-	211.15	52.79	0	52.79	0	52.79	105.57	211.15
O2 (m3/h)	-	-	1,266.9	316.72	266.56	50.16	42.22	7.94	15.89	31.78
Total Air (m3/h)	**-**	**-**	**7,038.31**	**1,759.58**	**1,591.56**	**168.02**	**85.80**	**82.21**	**164.43**	**328.86**

Compound/Stream	S-103	S-104 A, B, C, D	S-105 A, B, C, D	S-106 A, B, C, D	S-107 A, B, C, D	S-108 A, B, C, D	S-109 A, B	S-110
N2O	1.1%	1.1%	0%	11.9%	0%	24.3%	24.3%	24.3%
N2	77.9%	77.9%	83.3%	26.8%	50.8%	1.8%	1.8%	1.8%
CO2	3%	3%	0%	31.4%	0%	64.2%	64.2%	64.2%
O2	18%	18%	16.7%	29.9%	49.2%	9.7%	9.7%	9.7%
Total Air	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**

% (v/v)

Case 1:
N_2O production (24%) through a vacuum system

Base Equipament

MB – 101, 102 A to D: Membrane Modules
S – 101 to 110: Streams
VP – 101, 102 A to D: Vaccum Pumps

VOCs: Volatile Organic Compounds

Automatic Valves

FCV – 101 to 106: Flow Control Valves

Review Notes

Symbology

- Flow Control Valve
- Manual Valve (closed)
- 2-Way Flanged Valve
- 3-Way Flanged Valve
- Pipelines
- Electrical Signal

Control & Instrumentation

FIC: Flow Indicating Controller
FT: Flow Transmitter
TFI: Total Flow Indicating
TFT: Total Flow Transmitter

M: Motor

- **Instrument**
- **Shared Instrument**
- **Temperature Indicator**
- **Pressure Indicator**

N_2O Gas Purification
from Wastewater Treatment Plants

Flowsheet *Section 100*

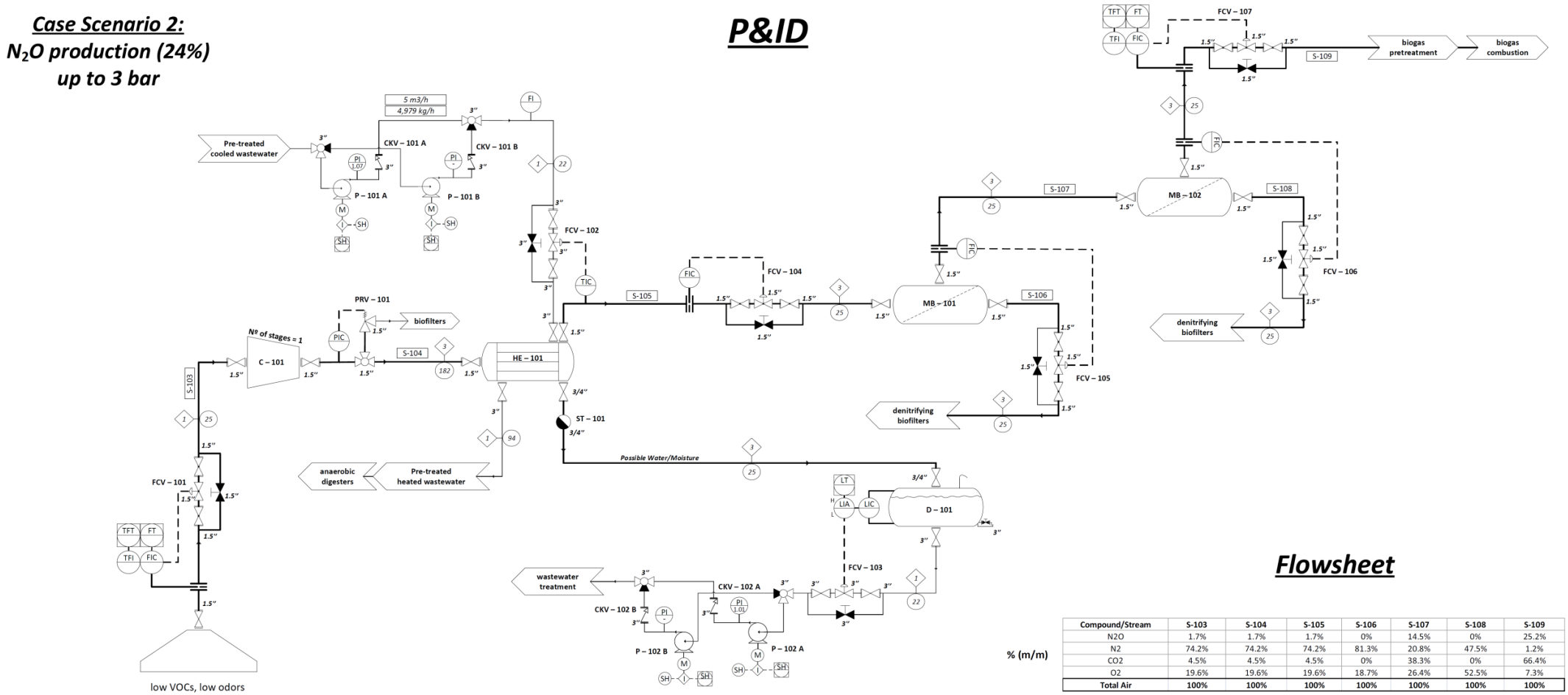
Margarida Martins nº 34158

March-23/2016

SINGLE-STAGE COMPRESSION	MEMBRANE MODULES

Case Scenario 2:
N_2O production (24%)
up to 3 bar

P&ID



Flowsheet

Compound/Stream	S-103	S-104	S-105	S-106	S-107	S-108	S-109
N2O	1.7%	1.7%	1.7%	0%	14.5%	0%	25.2%
N2	74.2%	74.2%	74.2%	81.3%	20.8%	47.5%	1.2%
CO2	4.5%	4.5%	4.5%	0%	38.3%	0%	66.4%
O2	19.6%	19.6%	19.6%	18.7%	26.4%	52.5%	7.3%
Total Air	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**

% (m/m)

Compound/Stream	S-101	S-102	S-103	S-104	S-105	S-106	S-107	S-108	S-109
N2O (kg/h)	-	-	143.9	143.9	143.9	0	143.9	0	143.9
N2 (kg/h)	-	-	6,275.1	6,275.1	6,275.1	6,068.7	206.4	199.6	6.8
CO2 (kg/h)	-	-	379.8	379.8	379.8	0	379.8	0	379.8
O2 (kg/h)	-	-	1,657.0	1,657.0	1,657.0	1,394.6	262.4	220.9	41.6
Total Air (kg/h)	**-**	**-**	**8,455.9**	**8,455.9**	**8,455.9**	**7,463.3**	**992.6**	**420.5**	**572.1**
TKN (kg-N/h)	**395.7**	**-**	-	-	-	-	-	-	-
TN (kg-N/h)	**-**	**212.5**	-	-	-	-	-	-	-
Physical state	Liquid	Liquid	Gas	Gas	Gas	Gas	Gas	Gas	Gas
Temperature (ºC)	22	22	25	182	25	25	25	25	25
Pressure (bar)	1.01	1.01	1.01	3	3	3	3	3	3

Compound/Stream	S-101	S-102	S-103	S-104	S-105	S-106	S-107	S-108	S-109
N2O (m3/h)	-	-	80	41.26	27.03	0	27.03	0	27.03
N2 (m3/h)	-	-	5,480.26	2,826.47	1,851.85	1,790.93	60.92	58.91	2
CO2 (m3/h)	-	-	211.15	108.9	71.35	0	71.35	0	71.35
O2 (m3/h)	-	-	1,266.9	653.41	428.1	360.30	67.80	57.06	10.74
Total Air (m3/h)	**-**	**-**	**7,038.31**	**3,630.04**	**2,378.33**	**2,151.23**	**227.10**	**115.97**	**111.13**

Compound/Stream	S-103	S-104	S-105	S-106	S-107	S-108	S-109
N2O	1.1%	1.1%	1.1%	0%	11.9%	0%	24.3%
N2	77.9%	77.9%	77.9%	83.3%	26.8%	50.8%	1.8%
CO2	3%	3%	3%	0%	31.4%	0%	64.2%
O2	18%	18%	18%	16.7%	29.9%	49.2%	9.7%
Total Air	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**

% (v/v)

Case 2:
N_2O production (24%)
up to 3 bar

Base Equipament

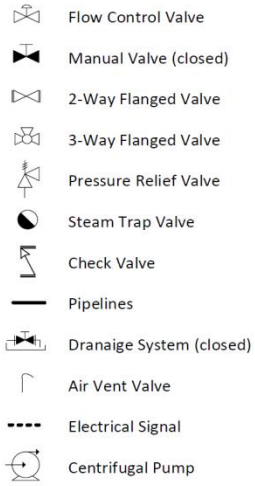
C – 101: Centrifugal Compressor
D – 101: Drum
HE – 101: Heat Exchanger
MB – 101, 102: Membrane Modules
P – 101, 102 A/B: Centrifugal Pumps
S – 101 to 109: Streams

VOCs: Volatile Organic Compounds

Automatic Valves

FCV – 101 to 107: Flow Control Valves
PRV – 101: Pressure Relief Valve
ST – 101: Steam Trap Valve
CKV – 101, 102 A/B: Check Valves

Symbology



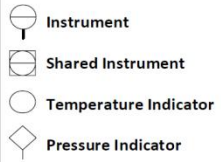
Control & Instrumentation

FI: Flow Indicator
FIC: Flow Indicating Controller
FT: Flow Transmitter
TFI: Total Flow Indicating
TFT: Total Flow Transmitter

PI: Pressure Indicator
PIC: Pressure Indicating Controller
TIC: Temperature Indicating Controller

LIC: Level Indicating Controller
LIA: Level Indicating Alarm (**H**igh, **L**ow)
LT: Level Transmitter

M: Motor
I: Interlock
SH: Net Positive Suction Head (NP**SH**)



N_2O Gas Purification
from Wastewater Treatment Plants

Flowsheet *Section 100*

Margarida Martins nº 34158

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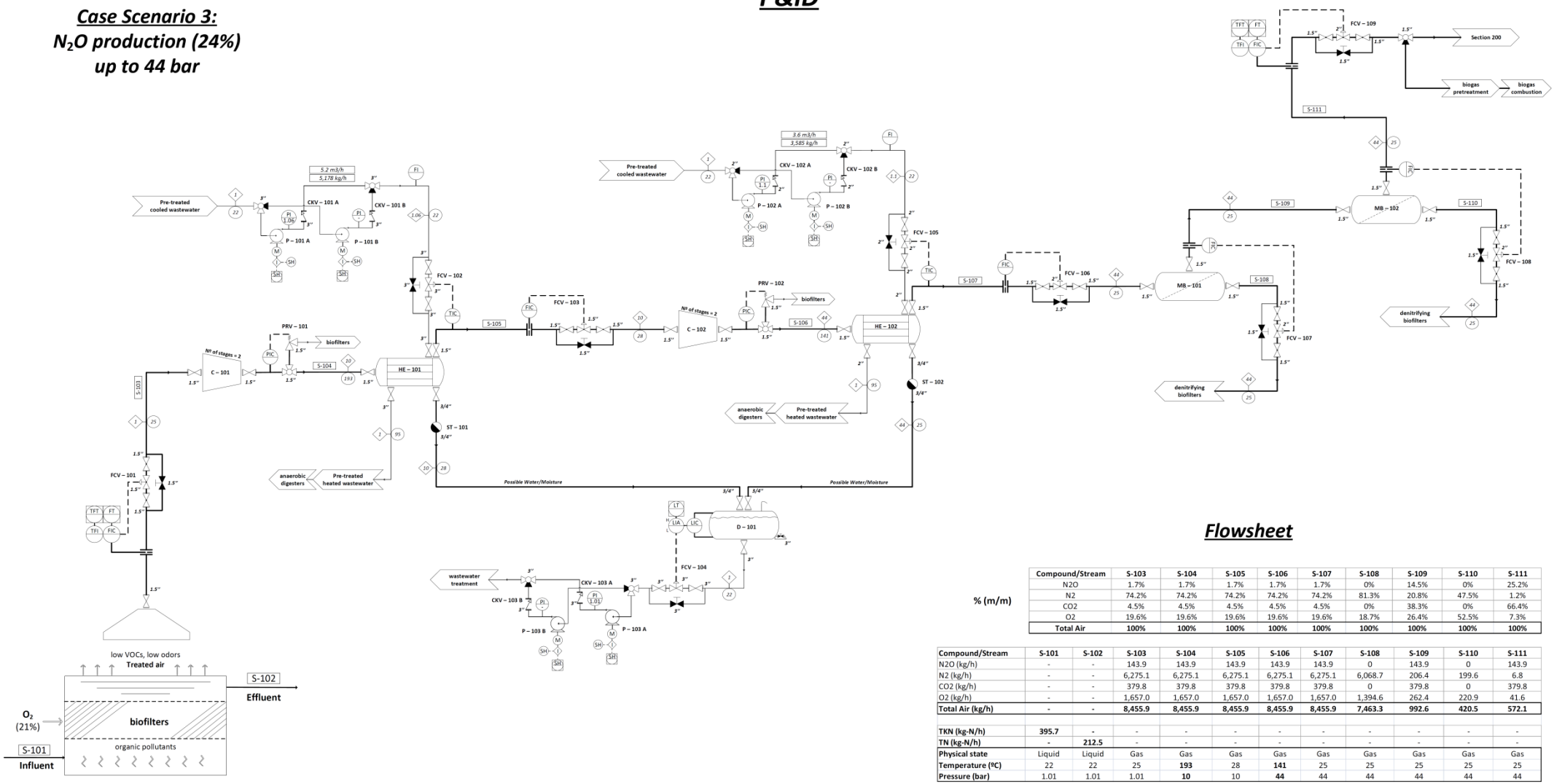
Review Notes

MULTI-STAGE COMPRESSION	MEMBRANE MODULES

Case Scenario 3:
N_2O production (24%)
up to 44 bar

P&ID



Flowsheet

% (m/m)

Compound/Stream	S-103	S-104	S-105	S-106	S-107	S-108	S-109	S-110	S-111
N2O	1.7%	1.7%	1.7%	1.7%	1.7%	0%	14.5%	0%	25.2%
N2	74.2%	74.2%	74.2%	74.2%	74.2%	81.3%	20.8%	47.5%	1.2%
CO2	4.5%	4.5%	4.5%	4.5%	4.5%	0%	38.3%	0%	66.4%
O2	19.6%	19.6%	19.6%	19.6%	19.6%	18.7%	26.4%	52.5%	7.3%
Total Air	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**

Compound/Stream	S-101	S-102	S-103	S-104	S-105	S-106	S-107	S-108	S-109	S-110	S-111
N2O (kg/h)	-	-	143.9	143.9	143.9	143.9	143.9	0	143.9	0	143.9
N2 (kg/h)	-	-	6,275.1	6,275.1	6,275.1	6,275.1	6,275.1	6,068.7	206.4	199.6	6.8
CO2 (kg/h)	-	-	379.8	379.8	379.8	379.8	379.8	0	379.8	0	379.8
O2 (kg/h)	-	-	1,657.0	1,657.0	1,657.0	1,657.0	1,657.0	1,394.6	262.4	220.9	41.6
Total Air (kg/h)	**-**	**-**	**8,455.9**	**8,455.9**	**8,455.9**	**8,455.9**	**8,455.9**	**7,463.3**	**992.6**	**420.5**	**572.1**
TKN (kg-N/h)	**395.7**	**-**	-	-	-	-	-	-	-	-	-
TN (kg-N/h)	**-**	**212.5**	-	-	-	-	-	-	-	-	-
Physical state	Liquid	Liquid	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Gas
Temperature (ºC)	22	22	25	**193**	28	**141**	25	25	25	25	25
Pressure (bar)	1.01	1.01	1.01	**10**	10	**44**	44	44	44	44	44

Compound/Stream	S-101	S-102	S-103	S-104	S-105	S-106	S-107	S-108	S-109	S-110	S-111
N2O (m3/h)	-	-	80	12.67	8.18	2.56	1.84	0	1.84	0	1.842
N2 (m3/h)	-	-	5,480.26	867.77	560.49	175.17	126.21	122.06	4.15	4.02	0.137
CO2 (m3/h)	-	-	211.15	33.43	21.6	6.75	4.86	0	4.86	0	4.863
O2 (m3/h)	-	-	1,266.9	200.61	129.57	40.49	29.18	24.56	4.62	3.89	0.732
Total Air (m3/h)	**-**	**-**	**7,038.31**	**1,114.47**	**719.83**	**224.97**	**162.09**	**146.61**	**15.48**	**7.9**	**7.574**

% (v/v)

Compound/Stream	S-103	S-104	S-105	S-106	S-107	S-108	S-109	S-110	S-111
N2O	1.1%	1.1%	1.1%	1.1%	1.1%	0%	11.9%	0%	24.3%
N2	77.9%	77.9%	77.9%	77.9%	77.9%	83.3%	26.8%	50.8%	1.8%
CO2	3%	3%	3%	3%	3%	0%	31.4%	0%	64.2%
O2	18%	18%	18%	18%	18%	16.7%	29.9%	49.2%	9.7%
Total Air	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**

Case 3:
N_2O production (24%)
up to 44 bar

Base Equipament

C – 101, 102: Centrifugal Compressors
D – 101: Drum
HE – 101, 102: Heat Exchangers
MB – 101, 102: Membrane Modules
P – 101 to 103 A/B: Centrifugal Pumps
S – 101 to 111: Streams

VOCs: Volatile Organic Compounds

Automatic Valves

FCV – 101 to 109: Flow Control Valves
PRV – 101, 102: Pressure Relief Valves
ST – 101, 102: Steam Trap Valves
CKV – 101 to 103 A/B: Check Valves

Symbology

- Flow Control Valve
- Manual Valve (closed)
- 2-Way Flanged Valve
- 3-Way Flanged Valve
- Pressure Relief Valve
- Steam Trap Valve
- Check Valve
- Pipelines
- Dranaige System (closed)
- Air Vent Valve
- Electrical Signal
- Centrifugal Pump

Control & Instrumentation

FI: Flow Indicator
FIC: Flow Indicating Controller
FT: Flow Transmitter
TFI: Total Flow Indicating
TFT: Total Flow Transmitter

PI: Pressure Indicator
PIC: Pressure Indicating Controller
TIC: Temperature Indicating Controller

LIC: Level Indicating Controller
LIA: Level Indicating Alarm (**H**igh, **L**ow)
LT: Level Transmitter

M: Motor
I: Interlock
SH: Net Positive Suction Head (NP**SH**)

- **Instrument**
- **Shared Instrument**
- **Temperature Indicator**
- **Pressure Indicator**

Review Notes

N_2O Gas Purification
from Wastewater Treatment Plants

Flowsheet *Section 100*

Margarida Martins nº 34158

March-23/2016

Case Scenario 3:
N_2O liquefaction (99.7%)

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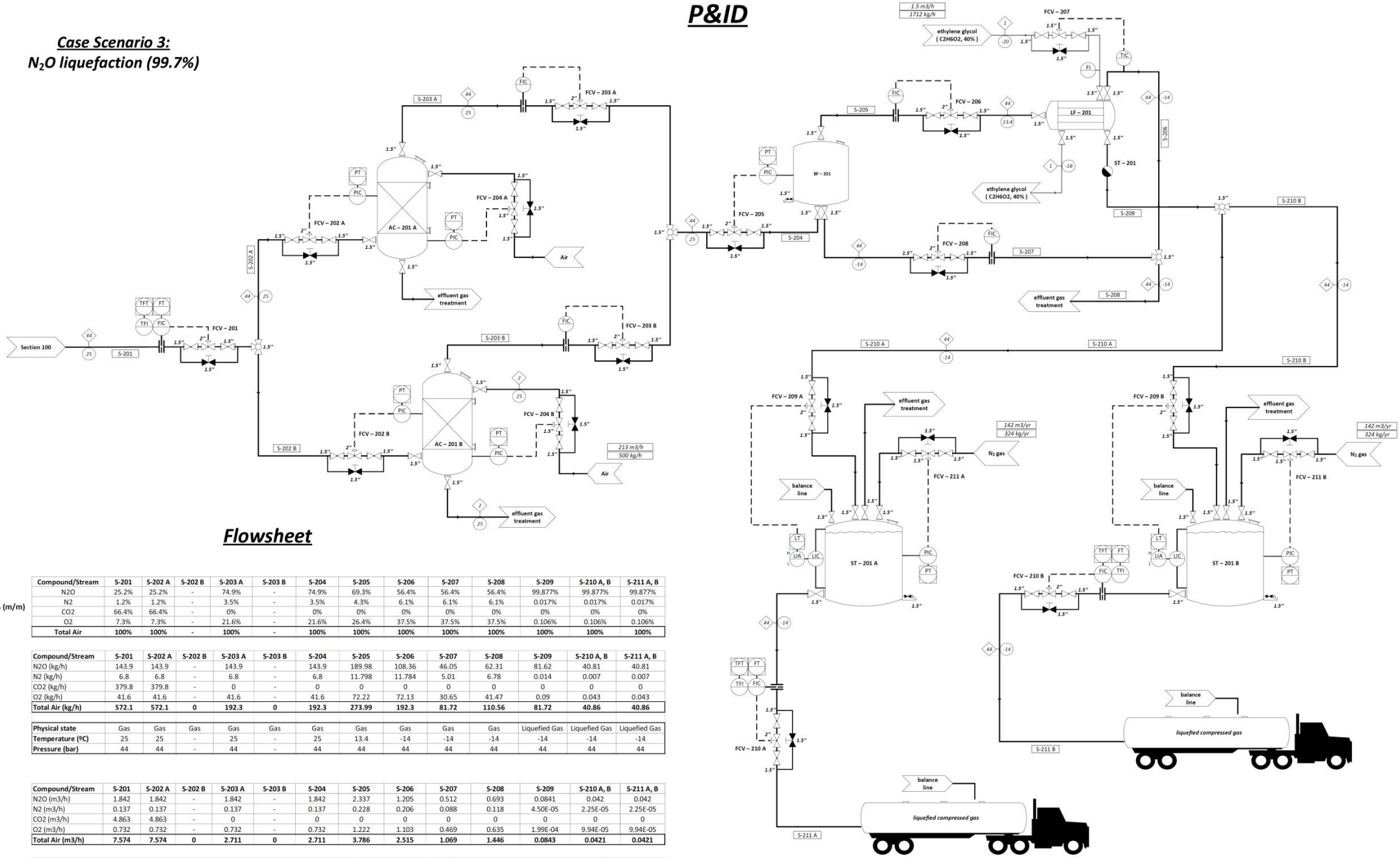

Flowsheet

Compound/Stream	S-201	S-202 A	S-202 B	S-203 A	S-203 B	S-204	S-205	S-206	S-207	S-208	S-209	S-210 A, B	S-211 A, B
% (m/m)													
N2O	25.2%	25.2%	-	74.9%	-	74.9%	69.3%	56.4%	56.4%	56.4%	99.877%	99.877%	99.877%
N2	1.2%	1.2%	-	3.5%	-	3.5%	4.3%	6.1%	6.1%	6.1%	0.017%	0.017%	0.017%
CO2	66.4%	66.4%	-	0%	-	0%	0%	0%	0%	0%	0%	0%	0%
O2	7.3%	7.3%	-	21.6%	-	21.6%	26.4%	37.5%	37.5%	37.5%	0.106%	0.106%	0.106%
Total Air	**100%**	**100%**	**-**	**100%**	**-**	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**

Compound/Stream	S-201	S-202 A	S-202 B	S-203 A	S-203 B	S-204	S-205	S-206	S-207	S-208	S-209	S-210 A, B	S-211 A, B
N2O (kg/h)	143.9	143.9	-	143.9	-	143.9	189.98	108.36	46.05	62.31	81.62	40.81	40.81
N2 (kg/h)	6.8	6.8	-	6.8	-	6.8	11.798	11.784	5.01	6.78	0.014	0.007	0.007
CO2 (kg/h)	379.8	379.8	-	0	-	0	0	0	0	0	0	0	0
O2 (kg/h)	41.6	41.6	-	41.6	-	41.6	72.22	72.13	30.65	41.47	0.09	0.043	0.043
Total Air (kg/h)	**572.1**	**572.1**	**0**	**192.3**	**0**	**192.3**	**273.99**	**192.3**	**81.72**	**110.56**	**81.72**	**40.86**	**40.86**
Physical state	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Liquefied Gas	Liquefied Gas	Liquefied Gas
Temperature (ºC)	25	25	-	25	-	25	13.4	-14	-14	-14	-14	-14	-14
Pressure (bar)	44	44	-	44	-	44	44	44	44	44	44	44	44

Compound/Stream	S-201	S-202 A	S-202 B	S-203 A	S-203 B	S-204	S-205	S-206	S-207	S-208	S-209	S-210 A, B	S-211 A, B
N2O (m3/h)	1.842	1.842	-	1.842	-	1.842	2.337	1.205	0.512	0.693	0.0841	0.042	0.042
N2 (m3/h)	0.137	0.137	-	0.137	-	0.137	0.228	0.206	0.088	0.118	4.50E-05	2.25E-05	2.25E-05
CO2 (m3/h)	4.863	4.863	-	0	-	0	0	0	0	0	0	0	0
O2 (m3/h)	0.732	0.732	-	0.732	-	0.732	1.222	1.103	0.469	0.635	1.99E-04	9.94E-05	9.94E-05
Total Air (m3/h)	**7.574**	**7.574**	**0**	**2.711**	**0**	**2.711**	**3.786**	**2.515**	**1.069**	**1.446**	**0.0843**	**0.0421**	**0.0421**

Compound/Stream	S-201	S-202 A	S-202 B	S-203 A	S-203 B	S-204	S-205	S-206	S-207	S-208	S-209	S-210 A, B	S-211 A, B
% (v/v)													
N2O	24.3%	24.3%	-	68.0%	-	68.0%	61.7%	47.9%	47.9%	47.9%	99.711%	99.711%	99.711%
N2	1.8%	1.8%	-	5.0%	-	5.0%	6.0%	8.2%	8.2%	8.2%	0.053%	0.053%	0.053%
CO2	64.2%	64.2%	-	0%	-	0%	0%	0%	0%	0%	0%	0%	0%
O2	9.7%	9.7%	-	27.0%	-	27.0%	32.3%	43.9%	43.9%	43.9%	0.236%	0.236%	0.236%
Total Air	**100%**	**100%**	**-**	**100%**	**-**	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**

Case 3:
N_2O liquefaction (99.7%)

Base Equipament

AC – 201 A/B: Adsorption Columns
BF – 201: Buffer Tank
LF – 201: Liquefier
ST – 201 A/B: Storage Tanks
S – 201 to 211 A/B: Streams

VOCs: Volatile Organic Compounds

Automatic Valves

FCV – 201 to 211 A/B: Flow Control Valves
ST – 201: Steam Trap Valve

Symbology

- Flow Control Valve
- Manual Valve (closed)
- 2-Way Flanged Valve
- 3-Way Flanged Valve
- Steam Trap Valve
- Manhole Door
- Pipelines
- Dranaige System (closed)
- Electrical Signal

Control & Instrumentation

FI: Flow Indicator
FIC: Flow Indicating Controller
FT: Flow Transmitter
TFI: Total Flow Indicating
TFT: Total Flow Transmitter

PT: Pressure Transmitter
PIC: Pressure Indicating Controller
TIC: Temperature Indicating Controller

LIC: Level Indicating Controller
LIA: Level Indicating Alarm (**H**igh, **L**ow)
LT: Level Transmitter

- **Instrument**
- **Shared Instrument**
- **Temperature Indicator**
- **Pressure Indicator**

Review Notes

N_2O Gas Purification
from Wastewater Treatment Plants

Flowsheet *Section 200*

Margarida Martins nº 34158

March-23/2016